Trialling stream rehabilitation tools to attenuate nitrate export and improve stream health in agricultural waterways

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For Pap – Clement C. Newcamp (1929 – 2008)

You shaped my work ethic and curiosity for the natural world, on the farm and in the water

and my Nephew – Lucas G. Goeller (2012 –)

You teach us that every day is a gift worth fighting for

"One of the penalties of an ecological education is that one lives alone in a world of wounds. Much of the damage inflicted on land is quite invisible to laymen. An ecologist must either harden his shell and make believe that the consequences of science are none of his business, or he must be the doctor who sees the marks of death in a community that believes itself well and does not want to be told otherwise."

Aldo Leopold (1949), 'A Sand County Almanac'

Contents

Abstract

Increased nutrient loading in agricultural drainage ditches and small streams caused by land-use intensification is a driver of global change and poses significant challenges for managing freshwater ecosystems globally. These headwater waterways can disproportionately influence downstream nutrient loads and ecosystem processes that affect nutrient cycling. I undertook this research within the Canterbury Waterway Rehabilitation Experiment in agricultural headwater waterways to: 1) characterize the hydrological and catchment-scale drivers of agricultural catchment nitrate loads, 2) implement nitrate removal tools targeting the key nutrient sources along the stream network, and 3) evaluate the in-stream and ecosystem-level impacts of stream rehabilitation. My findings highlight how nutrient loads in these lowland, spring-fed waterways can be highly dynamic, dominated more by groundwater than local run-off, and increase our general understanding of the scales and locations to implement nitrate loss rehabilitation tools. The substantial nitrate fluxes I measured from upstream springs, and from tile and open tributary drains, should be targeted for rehabilitation at the farm-scale to complement catchment-scale and land-based nitrate management. Therefore, I tested the suitability and performance of three small (< 30 m^3) edge-of-field denitrifying woodchip bioreactors implemented as part of a multi-tool, multi-scale, riparian rehabilitation programme. Rehabilitation enhanced downstream nitrate flux attenuation under losing stream hydrological conditions (i.e., decreasing discharge along the reach) post-rehabilitation, whereas there were no significant changes in this relationship over time in the control waterway. Therefore, hydrological variability not only drove waterway nitrate export, but also influenced the performance of riparian nitrate attenuation tools. To enhance in-stream nutrient removal and retention, I experimentally added woodchips to the channels of four waterways with low dissolved organic carbon and chronically-high nitrate. Substantial nitrate

depletions averaging 2.5 to 3.5 mg L^{-1} NO_3-N were manifested sporadically at different times and at different locations downstream of the wood addition. Soluble reactive phosphorus and dissolved organic carbon were also depleted in treatment reaches downstream of the wood, suggesting that I enhanced nutrient uptake as well as denitrification. Overall, my research advances current knowledge on the advantages of implementing multiple nutrient mitigation tools to accrue environmental benefits. I demonstrated how waterway nitrate mitigation efforts should focus on intercepting the groundwater, upstream, and drainage tributary pathways of nitrate fluxes and improving conditions to enhance nitrate removal along riparian zones and within waterways. The scale- and stressor-targeted approach that combines multiple rehabilitation tools is transferable to other agricultural headwater waterways impacted by multiple stressors and to situations where stream rehabilitation programmes must fit within working agricultural landscapes with limited space for natural water retention options or narrow riparian buffers to attenuate excess nutrients.

Plate 1. A spring-fed, agricultural headwater impacted by high nutrients, fine sediment, faecal bacteria, and weed macrophytes on the Canterbury Plains, South Island, New Zealand

Photo: Brandon C. Goeller

Chapter One:

General Introduction

Nutrient pollution from agricultural land use creates significant management challenges for rehabilitating freshwater ecosystems around the world (Glibert, 2017). Small waterways and ditches form the headwaters that drain agricultural landscapes and convey excess nutrients to downstream catchments (Dodds & Oakes, 2008; David, Drinkwater & McIsaac, 2010). Excess reactive nitrogen (N) and phosphorus (P) loading can cause eutrophication, toxic algal blooms, anoxic dead zones, altered food webs, and nitrate toxicity in groundwater (Glibert, 2017). In light of the cumulative effects of agricultural land use expansion and intensification to feed the world's growing population, as well as climate change and industrialization, the damaging human health and environmental consequences of excess nutrient loading are likely to increase (Rabalais *et al.*, 2009). Therefore, sustainable management of agricultural lands and freshwater ecosystems is required to meet anthropogenic food, fibre, and fuel demands into the future (Pretty *et al.*, 2010; Lammers & Bledsoe, 2017).

Managing N is particularly problematic and challenging because the same atom of N can have differing effects across ecosystems as it is transformed along the biogeochemical pathways known as the nitrogen cascade (Galloway *et al.*, 2003, 2008) (Figure 1.1). However, the complex mechanisms that govern the flow and standing stocks of N in streams have been extensively studied and are reasonably well understood (Birgand *et al.*, 2007; Lammers & Bledsoe, 2017). Under typical conditions, the most common N species — inorganic N, including nitrate-nitrogen (NO_3-N) and ammonium-nitrogen (NH_4-N) — are generally present in low concentrations (Galloway *et al.*, 2003). Inorganic N often associated with undisturbed, headwater catchments originates from terrestrially-derived organic N that enters the system as detritus or dissolved organic matter (Bernot & Dodds, 2005). However, agricultural land-use generates a substantial and problematic source of excess inorganic N, particularly nitrate-nitrogen (Birgand *et al.*, 2007). Nitrate-nitrogen is the most mobile form of N in soils and water, and it is biologically available for uptake by primary producers. In contrast, ammonium-nitrogen is less prevalent in the water column because it adsorbs to fine sediment or is nitrified (i.e., converted to nitrite-nitrogen, NO_2-N, and nitrate-nitrogen), but it is also highly bio-available. Excess inorganic N can be removed from the system by conversion to nitrogen-oxides (NO_x) and atmospheric nitrogen (N_2) via denitrification by heterotrophic microbes, or it is readily assimilated into biomass by algae and aquatic plants, making it less bio-available (Peterson *et al.*, 2001). Because inorganic N can limit primary production in freshwater ecosystems and can be tightly spiralled through aquatic food webs (Vanni, 2002; Ensign & Doyle, 2006), excess nitrate is especially problematic. Furthermore, agricultural intensification and shifts to N-saturated terrestrial ecosystems has followed widespread losses of organic carbon sources due to deforestation and land clearance (Stutter *et al.*, 2018). These missing carbon sources that fuel microbially-mediated retention and removal of inorganic N exacerbate the problematic flow of inorganic N flow through coupled terrestrial and aquatic ecosystems (Schlesinger, 2009).

Given the transport and fate of N across and within ecosystems, spatially- and temporally-variable fluxes of nitrate are commonly characterised across agricultural land and within waterways (Gentry *et al.*, 2009). Agricultural, headwater catchments are further supplemented by fluxes of excess nitrate leached from soils and into artificial drainage networks via subsurface tiles, open tributary drains, and springs and seeps, which bypass denitrification zones in shallow groundwater and riparian buffers (Jaynes & Isenhart, 2014; Williams, King & Fausey, 2015b). Characterising nitrate stocks and pathways or flows in small agricultural catchments can be perplexing and require intensive sampling across a waterway network over time to best capture how fluxes can change with different sources of N inputs along the stream network and from changes in land management (Williams *et al.*, 2015d).

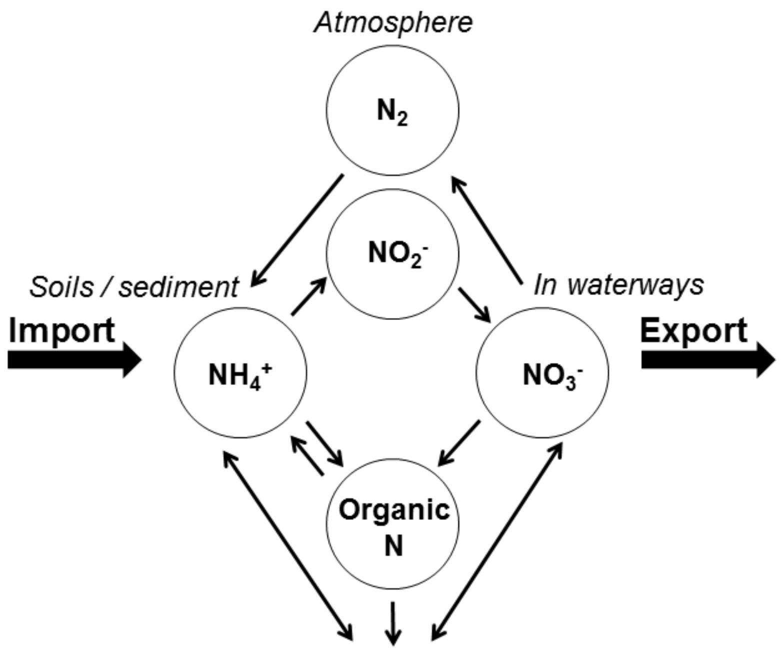

Figure 1.1 The nitrogen cycle, with arrows representing N transformations based on Bernot and Dodds (2005).

Once N is transported into waterway networks, the inherent ability of agricultural streams and ditches to cycle and attenuate nutrients is limited (Royer, Tank & David, 2004; Kröger *et al.*, 2007). This is largely due to their channelized nature and the overall lack of complex structures such as large wood, riffles, and pools that promote contact with the benthos and create low oxygen environments required for denitrification (Lazar *et al.*, 2014; McPhillips *et al.*, 2015). Moreover, the extent of stream N loading and deficient organic carbon sources (carbon limitation) impairs fundamental stream ecosystem process of microbial activity causing leaf and wood breakdown (Woodward *et al.*, 2012), affecting N retention and processing (Mulholland & Webster, 2010; Stutter *et al.*, 2018), invertebrate productivity (Cross *et al.*, 2006), and stream metabolism (Tank *et al.*, 2010; Burrell *et al.*, 2014). Although waterways impacted by agricultural land use can have higher biological activity linked to nutrient cycling (Bernot *et al.*, 2006), biotic assimilation and uptake approach saturation as nitrate concentrations in the water column increase (Bernot & Dodds, 2005; Earl, Valett & Webster, 2006). Royer et al. (2004) found nitrate uptake velocities, the rates at which nitrate molecules leave the water column, were lower in agricultural headwater streams compared to undisturbed streams. Moreover, those same agricultural waterways exported more nitrate than was removed by denitrification. Thus, agricultural waterways receiving high N loads may often have impaired abilities to remove N across a variety of pathways, especially when they have limited or insufficient organic matter to support nutrient cycling (Stutter *et al.*, 2018). Overall, this situation highlights the need for interventions to enhance the key N transformations to attenuate excess nitrate-nitrogen in agricultural waterways.

Compared to larger waterways, small waterways can have increased N transformation and cycling rates due to increased contact between stream water and the benthos (Bernot & Dodds, 2005; Findlay *et al.*, 2011). Hence, small waterways should be ideally suited for stream rehabilitation tools to attenuate nitrate export (Craig *et al.*, 2008; Feld *et al.*, 2018). The responsiveness of small waterways to rehabilitation actions, as well as the disproportionate abundance and influence of headwaters on water quality and ecosystem processes at larger spatial scales, makes headwater nutrient rehabilitation a potentially effectual management approach (Alexander *et al.*, 2007; Thomas, 2014). Implementing riparian and in-stream N attenuation tools in agricultural headwaters may improve water quality, habitats, and biological diversity downstream (Meyer *et al.*, 2007; Dodds & Oakes, 2008). Therefore, stream rehabilitation tools to mitigate the deleterious effects of N loading in aquatic environments are recommended to complement fertilizer reductions and other land-based nutrient source controls and best management practices (Craig *et al.*, 2008; Faust *et al.*, 2017). However, despite opportunities to address headwater nutrient loads with complementary land- and stream-based management and rehabilitation with multiple tools implemented across these scales, in practice, these are seldom combined (Tomer *et al.*, 2013; Kröger *et al.*, 2015).

In contrast to traditional stream restoration (i.e., structural restoration of woody debris, riparian planting, etc.), functionally-based stream rehabilitation actions can focus on enhancing retention, removal, and biological transformation of N in riparian zones, stream banks, and stream channels (Craig *et al.*, 2008; Faust *et al.*, 2017). Other than providing the correct hydrological and biochemical conditions to enhance nutrient cycling, nitrate-removal tools could be, yet rarely are, strategically implemented to intercept sources of high nitrate along and within waterways, such as subsurface tiles and open tributary drains. This is perhaps due to the lack of evidence and substantial uncertainties on the spatial and temporal scales/variable nature of nitrate fluxes (Williams *et al.*, 2015d), which likely hinder scaling-up rehabilitation within catchments. Moreover, nutrients, fine sediment, and water diversions and abstractions interact as multiple stressors which affect stream ecosystems draining agricultural landscapes (Allan, 2004; Matthaei, Piggott & Townsend, 2010). Due to these multiple-stressor impacts, N attenuation tools applied singly may have finite capacity to address agro-environmental sustainability by themselves and may provide limited ecosystem services (Christianson *et al.*, 2014). Moreover, each of these tools has specific implementation and performance constraints (Craig *et al.*, 2008). Therefore, procuring optimal nutrient cycling and water quality benefits from stream rehabilitation requires the development of stream restoration options (i.e., a 'toolbox') that operate at different scales, seek to address the variability around N transformations, and can therefore be implemented with reasonable or improved certainty and success. Accounting for the underlying hydrological variability and contributions from key sources within the waterway network may be the largest driver of the processes needed to enhance N-cycling and influence in-stream nutrient loads. Thus far, this has been a limitation identified in previous studies (Mulholland & Hill, 1997; Royer *et al.*, 2004; Filoso & Palmer, 2011). Combining multiple stream rehabilitation tools across the key locations in the stream network challenges the common, one-size-fits all approach, which has often failed to procure benefits to improving downstream nutrient loads (Filoso & Palmer, 2011; Doyle & Shields, 2012).

The development and implementation of stream rehabilitation actions requires effective translation of the complex science for landowners/end-users, who in turn can inform and co-develop management solutions with scientists and practitioners (Enquist *et al.*, 2017). Furthermore, landowner co-development of stream rehabilitation solutions could enhance the uptake of these tools (Rhodes, Closs & Townsend, 2007; Hallett *et al.*, 2017). Although nitrate-removal tools and functionally-based restoration approaches are becoming prominent features in stream restoration (Newcomer Johnson *et al.*, 2016; Faust *et al.*, 2017), tools are often implemented singly and evaluated in isolation within catchments (Kröger *et al.*, 2015). Given the variable source pathways, transport, and fate of nutrient delivery within and through agricultural catchments, evidence is needed to show how multiple tools in a 'toolbox' might address the prevailing sources of nutrient loss in a complementary fashion along and within waterways. Here, the rehabilitation 'toolbox' refers to a collection of nitrate attenuation options that are evidence-based and can be implemented in a specific context. We expect a toolbox-approach to accrue the most benefits for stream rehabilitation programmes, but further evidence is needed to show how multiple, or different, tools can be implemented at the farm-scale to attenuate catchment nitrate. Therefore, a fundamental objective and knowledge gap addressed by my research was to co-develop, trial, and evaluate nitrate-removal tools that were implemented within a stream rehabilitation toolbox-approach to match the sources and variability in nitrate-nitrogen fluxes along the waterway network to attenuate in-stream nitrate.

Thesis Organisation

I undertook the research for this PhD thesis within the Canterbury Waterway Rehabilitation Experiment, a long-term, collaborative research programme that tested practical tools to target multiple stressors in nine small waterways on the agriculturally-dominated Canterbury Plains of the South Island, New Zealand (CAREX, http://www.carex.org.nz). Over the course of CAREX, waterway management tools, such as improving riparian zones, removing fine sediment, managing aquatic macrophytes, and removing nutrients were experimentally tested. My objectives within CAREX were to: 1) characterize the hydrological and catchment-scale drivers of agricultural waterway nitrate loads, 2) implement nitrate-removal tools targeting the key nutrient sources along the stream network, 3) evaluate the in-stream and ecosystem-level impacts of stream rehabilitation, and 4) contribute to the development and demonstration of a toolbox-based stream rehabilitation approach that is transferable to other small agricultural waterways. I have written this thesis as a series of stand-alone manuscripts for publication, with each chapter fulfilling part of the overall thesis objectives. The thesis chapters and key outputs pertaining to the overarching objectives are detailed next. In Chapters Two, Three, Four, and Five, I refer to "we", since these chapters will be co-authored work submitted for publication.

Chapter Two, "Thinking beyond the bioreactor box: incorporating stream ecology into edge-of-field nitrate management", is a published literature review on the factors affecting the potential of denitrifying bioreactors to improve stream health and ecosystem services in small agricultural waterways (Goeller *et al.*, 2016). This review identifies knowledge gaps and discusses the potential follow-on effects of edge-of-field denitrification bioreactors on stream ecosystem function. Chapter Two also reveals that nitrate-management with engineering-based tools has been oversimplified and lacks a functional or ecological approach to manage the inherently variable N transformations along and within waterways. Therefore, Chapter Two synthesizes and links bodies of literature from agricultural engineering and drainage water management with studies of stream ecosystem function and rehabilitation, providing an ecological framework for evaluating nitrate-loss mitigation tools.

Chapter Three, “Springs drive downstream nitrate export from artificially-drained agricultural headwater catchments”, characterizes the overall influence of catchment hydrology and the relative contributions from upstream springs and edge-of-field sources on downstream nitrate export. Four years of data from the nine CAREX waterways spanning a gradient of nitrate loads were analysed to elucidate the important scales and sources of nitrate loads to address farm-scale nutrient management strategies at critical source areas, which contribute disproportionately to downstream nitrate flux. This is one of the first studies to measure and compare replicated farm- and catchment-scale sources of nitrate export for multiple waterways over multiple years. The insights from this work established the timing and relative contributions of springs and tributaries, tile- and surface drains, to downstream nitrate fluxes within catchments to inform management and rehabilitation approaches to attenuate downstream N loss.

Given the key influences of waterway hydrology and edge-of-field nutrient fluxes on catchment nitrate loads in Chapter Three, Chapter Four, “Small-scale denitrifying woodchip bioreactors combined with riparian rehabilitation enhance agricultural waterway nitrate flux attenuation, but only at low flows”, presents evidence of multiple-tool, multiple-scale riparian rehabilitation actions to attenuate downstream nitrate. In a three-and-a-half-year trial, riparian rehabilitation and edge-of-field bioreactors enhanced reach nitrate-nitrogen flux attenuation compared to pre-rehabilitation attenuation, but only under relatively low flow conditions. In both the control and treatment waterways at all times, nitrate-nitrogen fluxes increased when reaches gained water downstream. Because a substantial portion of the in-stream N load was not removed by riparian rehabilitation tools, my research also examined in-stream tools to enhance nutrient retention and removal within the stream network.

Chapter Five, “Adding in-stream wood enhances removal of nitrate, but only sporadically, in spring-fed, agricultural headwaters”, addresses the largest N load, which was in-stream, by experimentally altering the standing stock of organic matter to boost nutrient retention and removal. This was a large-scale experiment replicated in paired 400 m upstream control and treatment reaches downstream of a wood addition in four waterways with low dissolved organic carbon and high nitrate-nitrogen concentrations. The wood added organic matter and provided substrate for microbial nutrient cycling, which was manifested sporadically in spatially- and temporally-variable depletions in nitrate, soluble reactive phosphorus, and dissolved organic carbon in treatment reaches downstream. Overall, Chapter Four and Chapter Five suggest that combining or ‘stacking’ N-removal tools at multiple scales in and along the stream network can enhance catchment N attenuation.

Finally, Chapter Six, “Synthesizing stream nutrient removal and rehabilitation insights to improve agricultural waterway management” weaves together the scientific insights and management implications produced by this thesis to improve agricultural waterway nutrient management and rehabilitation. These insights show how quantifying the variability in nitrate-nitrogen pathways offers evidence for a multi-layered approach to attenuate downstream nitrate. Revealing the multiple influential locations and the influences of hydrological variability and other factors, such as carbon-limitation, that should be addressed with rehabilitation actions, underpins the notion that there is no one-size-fits-all approach to waterway nutrient management. Also, because the ecosystem processes linked to nutrient retention and removal in these waterways are inherently variable and impacted by multiple stressors, incorporating the variability of multiple stream ecosystem responses over different spatial and temporal scales is essential to rehabilitating these waterways. This capstone also features the practical science communication outputs that helped this project contribute to the overall impact of CAREX to collaboratively develop solutions to address the multi-scale, multi-stressor issues in agricultural catchments.

Plate 2. Journal cover of JEQ special section 'Moving denitrifying bioreactors beyond proof of concept,' showing construction of a woodchip bioreactor on a New Zealand dairy farm

Photo: Brandon C. Goeller

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Co-Authorship Form

This form is to accompany the submission of any thesis that contains research reported in co-authored work that has been published, accepted for publication, or submitted for publication. A copy of this form should be included for each co-authored work that is included in the thesis. Completed forms should be included at the front (after the thesis abstract) of each copy of the thesis submitted for examination and library deposit.

Please indicate the chapter/section/pages of this thesis that are extracted from co-authored work and provide details of the publication or submission from the extract comes:

Chapter Two "Thinking beyond the bioreactor box: incorporating stream ecology into edge-of-field nitrate management"

Goeller, B.C., C.M. Febria, J.S. Harding, and A.R. McIntosh. 2016. Thinking beyond the bioreactor box: incorporating stream ecology into edge-of-field nitrate management. J. Environ. Qual. 45(3): 866–872.

Please detail the nature and extent (%) of contribution by the candidate:

Brandon is the first author on this published literature review. He conceived the idea for this publication, identified the key knowledge gaps, carried out the literature review, and synthesized the findings of the literature review into a peer-reviewed journal article. He wrote the first draft of the text and likely wrote 90% of the text as a whole.

Certification by Co-authors:

If there is more than one co-author then a single co-author can sign on behalf of all

The undersigned certifys that:

- The above statement correctly reflects the nature and extent of the PhD candidate's contribution to this co-authored work
- In cases where the candidate was the lead author of the co-authored work he or she wrote the text

Name: *Angus McIntosh* Signature: Date: *16 June 2018*

Chapter Two:

Thinking beyond the bioreactor box: incorporating stream ecology into edge-of-field nitrate management

Goeller, B.C., Febria C.M., Harding J.S. & McIntosh A.R. (2016) Thinking beyond the bioreactor box: incorporating stream ecology into edge-of-field nitrate management. *Journal of Environment Quality* 45, 866–872.

Introduction

Land-use expansion and intensification of agroecosystems are major drivers of contemporary global change, especially for stream ecosystems (Vörösmarty *et al.*, 2010). Anthropogenic loading of reactive nitrogen (N) to streams and rivers has indirectly altered biodiversity, community structure, and ecosystem functioning via changes in primary productivity across aquatic ecosystems worldwide (Smith, Tilman & Nekola, 1999). Reactive nitrogen encompasses all biologically, photochemically, and radioactively active nitrogen (N) compounds in the lithosphere, biosphere, and atmosphere. In light of the cumulative effects of climate change, expanding industrialization, and increasing land conversion for agriculture to feed the world's growing population, N generation is likely to increase (Galloway *et al.*, 2008). Therefore, addressing agriculturally-derived N affecting interconnected freshwater ecosystems across spatial and temporal scales poses urgent and critical challenges for science, management, and policy.

Agricultural land-use pressures, especially nutrient pollution from excess N, transcend farm boundaries, possibly creating high external costs downstream (Foote, Joy & Death, 2015). In agricultural streams, the formation of toxic algal blooms, hypoxia, and altered structure of eutrophic food webs are common but complex challenges to address (Dodds *et al.*, 2009). An extreme example of watershed eutrophication is manifested in anoxic dead zones in river deltas and estuaries worldwide. These are prime examples of the economic, social, and ecological costs of excess N loading and export from agricultural watersheds (Diaz & Rosenberg, 2008).

Here, we focus our discussion on nitrate-nitrogen (NO_3-N) remediation but acknowledge that nutrients, fine sediment, and water diversions and abstractions interact as multiple stressors affecting agricultural streams (Matthaei *et al.*, 2010). The cumulative effects of agricultural land-use pressures have led to aquatic habitat loss and fragmentation, which has decreased freshwater biodiversity and deleteriously shifted the provisioning of ecosystem services (Stokstad, 2005). Specifically, land conversion for agriculture, land drainage for food production, and wetland and riparian forest losses have spatially decoupled N inputs from sites of denitrification and assimilation, altering the regulation of runoff, erosion, water purification, and nutrient cycling (Arango & Tank, 2008).

Small agricultural streams, including drainage ditches, are the headwaters of larger streams and rivers, acting as potential sources of N to downstream watersheds. Although small streams generally support higher rates of denitrification because of their greater surface area relative to discharge (Peterson *et al.*, 2001), the intrinsic ability of agricultural streams to support N removal via denitrification appears to be severely limited (Kröger *et al.*, 2007), likely due to channelization and the overall lack of complex structures such as large wood, riffles, and pools that support denitrifying conditions (Lazar *et al.*, 2014). Thus, improving in-stream conditions to take advantage of the inherent propensity of small streams to perform denitrification will be important.

In many agricultural landscapes, artificial sub-surface tile drains are also used to remove excess water. Although tile drains can reduce the loss of sediment and sediment-bound nutrients and pathogens to streams, they increase the movement of water-soluble nitrate-nitrogen to stream networks (Skaggs, Fausey & Evans, 2012). Furthermore, subsurface drainage networks bypass potential N removal zones in riparian buffers and anaerobic groundwater (Kellogg *et al.*, 2005). Therefore, even when farmers adopt best management practices (BMPs), significant amounts of nitrate-nitrogen can be exported downstream because of this enhanced waterway connectivity and limited riparian and in-stream denitrification capacity (David *et al.*, 2010).

Edge-of-field N removal tools are implemented along or within the riparian zone to reduce excess nutrients from entering streams. For example, denitrifying bioreactors implemented at the edge-of-fields mimic the nitrate-nitrogen loss expected from denitrification in riparian buffers and wetlands, and they can mitigate the harmful effects of excess N in human-dominated landscapes (Schipper et al., 2010a). Bioreactors are typically woodchip-filled excavations that promote anaerobic redox conditions to remove N from tile drain effluent before it is discharged to agricultural streams. Moreover, bioreactors have the advantages of not removing land from agricultural production, they can be designed to treat nitrate-nitrogen loads under a variety of flow and loading conditions during all seasons, and they are compatible with other N management tools (Christianson, Bhandari & Helmers, 2012a). Given that food production needs to be maintained, it is likely these tools will play a potentially useful role in meeting N-management targets to protect human and freshwater health.

Although the performance of bioreactors to enhance N removal via denitrification has been described in reviews (Schipper *et al.*, 2010b; Christianson *et al.*, 2012a) and evaluated with meta-analysis (Addy *et al.*, 2016), linkages between the engineering, biogeochemistry, and subsequent effects on stream ecology could be better developed. Unfortunately, the paucity of data on the stream health and ecosystem service benefits of bioreactors precludes a quantitative meta-analysis of their impacts. This information is needed to facilitate the implementation of bioreactors, optimize adaptive working solutions, inform strategies to manage N pollution, and maximize stream ecosystem health.

Here, we expand the discussion around bioreactor implementation to include factors affecting their influences on stream ecology and stream health, and we identify knowledge gaps to investigate in future assessments of bioreactor performance. First, we evaluate the factors potentially influencing bioreactor performance and subsequent impacts on stream health. Next, we outline how bioreactors might contribute to farm- and watershed-scale management to improve the functioning and ecological services of agricultural streams. Finally, we describe the ecological monitoring needed to elucidate the stream health benefits of bioreactors.

Linking bioreactor performance with stream ecosystem health in agricultural landscapes

The ability of bioreactors to enhance N removal via denitrification is well documented and depends on several variables, including: (i) tile drain flow rate, dissolved oxygen concentrations, and permeability within the bioreactor, including hydraulic residence time and redox conditions, (ii) bioreactor media, for example carbon source, and (iii) influent nitrate-nitrogen concentrations, water temperature, and microbial communities, which influence the denitrification reaction rate (Christianson *et al.*, 2012a). The sustained nitrate-nitrogen removal rates for bioreactors using wood media vary from 2 - 22 g N m^{-3} day^{-1}, and field-scale bioreactors have been found to reduce annual nitrate-nitrogen loads from tile drainage by 12 – 98 % in case studies (Woli *et al.*, 2010; Christianson *et al.*, 2012b; David *et al.*, 2015). There is evidence that bioreactors may also be effective in removing fecal bacteria and environmental pathogens from subsurface drainage (Jamieson *et al.*, 2002).

Pollution swapping in bioreactors has the potential to release methyl mercury, poisonous hydrogen sulphide (H_2S), greenhouse gasses (nitrous oxide N_2O, methane CH_4, carbon dioxide CO_2), and high dissolved organic carbon (DOC), which increases biological oxygen demand (BOD) (Christianson *et al.*, 2012a; Healy *et al.*, 2012). Field and laboratory evidence of the pollution swapping potential when bioreactor nitrate-nitrogen concentrations drop below 0.5 mg L^{-1} and as redox potential increases show that bioreactor performance and environmental quality are interdependent (Warneke *et al.*, 2011b; Healy *et al.*, 2012; Weigelhofer & Hein, 2015). However, if designed carefully to match field conditions, bioreactors may have lower risk of environmental pollution swapping. For example, (Elgood *et al.*, 2010) reported average annual N_2O and CH_4 emission rates of 2.4 mg N m^{-2} d^{-1} and 297 mg C m^{-2} d^{-1}, respectively, from an in-stream bioreactor, which were comparable to emissions produced by croplands, nitrate-polluted rivers, or reservoirs. (Weigelhofer & Hein, 2015) recommend investigations of the positive and negative stream health impacts of bioreactors to facilitate comparisons of treated versus untreated agricultural waterways. There is a tradeoff in achieving N removal in bioreactors without promoting a strong enough residence time or redox gradient in bioreactors for pollution swapping to occur; this can be achieved by designing bioreactors to ensure that nitrate is the terminal electron acceptor. Bioreactor effluent should also not impair, but rehabilitate fundamental stream ecosystem processes.

Designing and managing bioreactors to optimize N removal and to provide potential stream health and ecosystem service environmental benefits are intrinsically linked. For example, the degree of N loading impacts woodchip breakdown and denitrification rates in bioreactors, as well as coarse particular organic matter (CPOM) breakdown in streams. Leaf and wood CPOM breakdown is a fundamental stream ecosystem process, affecting N retention and processing, invertebrate productivity, and stream metabolism (Allan & Castillo, 2007). Also, high levels of nitrate-nitrogen in stream water can decrease the rate at which N is removed via assimilation and uptake (Bernot & Dodds, 2005). Accordingly, as bioreactors remove N from agricultural drainage, changes in the rate of organic matter breakdown, stream denitrification rates, N uptake and assimilation by in-stream primary producers, and N uptake and assimilation by benthic invertebrate and fish consumers may be expected. Changing organic matter processing and primary production will almost certainly have consequences for stream secondary and tertiary production and food web characteristics as well. Because 0.5 - 1.0 mg TN (total nitrogen) L^{-1} can cause adverse effects of eutrophication (Camargo & Alonso, 2006) and 2 - 10 mg NO_3-N L^{-1} impairs sensitive freshwater fish, amphibians, and benthic invertebrates (Camargo, Alonso & Salamanca, 2005; Hickey, 2013), bioreactor performance needs to be matched to N loading conditions to improve agricultural stream health. This may require several bioreactors installed along a stream network to obtain stream NO_3-N concentrations that are within or below ecologically-meaningful limits.

Bioreactors may be seen to have little influence on stream health when other stressors, especially fine benthic sediment, are also present and suppressing stream health. For example, low-gradient streams that receive high loads of sediment finer than 2 mm can reduce the performance of bioreactors installed directly into the stream bed (in-stream designs) by reducing the permeability of the porous bioreactor media and by impacting hydraulic residence time (Robertson & Merkley, 2009). By smothering the streambed and reducing linkages between surface water and groundwater, fine sediment loading also impairs benthic invertebrate and fish assemblages in agricultural streams (Burdon, McIntosh & Harding, 2013). Thus, stream riparian protection measures which prevent fine sediment entry need to be in place if expected benefits from bioreactors are actually to accrue. Also, implementing in-stream bioreactors with sediment traps or two-stage channels may benefit stream health by reducing inputs of N and fine sediment synergistically, as well as improving habitat for benthic invertebrates and fish.

If stream flow regimes associated with 'flashy' tile drain flows are severe, bioreactors should not be expected to contribute to stream health recovery, since stream biota will be limited by stressors other than nitrate-nitrogen. Besides nitrate-nitrogen loading, winter temperatures and the frequency and intensity of precipitation can be major limits to bioreactor performance (David *et al.*, 2015), and by influencing the natural flow regime, flows are also key drivers of biological activity and ecological interactions in streams (Lytle & Poff, 2004). Especially in semi-arid regions or during droughts, the frequency and duration of flow events underpins bioreactor performance (Christianson, Hanly & Hedley, 2011; Christianson *et al.*, 2012a) and the activity of stream microbes, including denitrifying bacteria (Merill & Tonjes, 2014). Assessing N removal under highly variable precipitation, hydrological, and site conditions is necessary to improve the performance of N mitigation tools (Koch *et al.*, 2014), and these environmental factors also influence stream ecosystem functioning. To better predict the impacts of bioreactor effluent on the physico-chemical and biological health of agricultural streams, improved understanding of field-scale bioreactor performance under variable nitrate-nitrogen loading, tile drain flow, and temperature regimes is needed (Christianson *et al.*, 2012a).

Quantitative data on the influence of bioreactors on stream health are needed to inform management decisions, and they may also help disentangle the pervasive effects of excess N loading on the structure and function of stream communities in multiple stressor environments. Evaluations of field-scale bioreactors should characterize to what extent bioreactor performance might improve agricultural stream health and ecosystem services. We have identified several knowledge gaps that need to be addressed to assess the effectiveness of bioreactors: (i) can bioreactors reduce in-stream nitrate-nitrogen concentrations significantly to improve stream health, for example by reducing algae and macrophyte growth, preventing excessive microbial activity, and supporting eutrophication-sensitive invertebrates and fish, (ii) do bioreactors negatively impact downstream water chemistry (e.g., create anoxic conditions, release sulphates, heavy metals, or methyl mercury), and (iii) are there other ecological consequences of bioreactors which might influence ecosystem structure, function, and services? We recommend that if bioreactors are to positively impact the health of agricultural streams, then nitrate-nitrogen loads and other key bioreactor performance factors need to be managed within meaningful biological limits to rehabilitate stream ecosystem structure and function.

Strategic roles and evaluation of bioreactors in farm-scale and watershed-scale N management

Given the multiple goals of stream management and environmental policies around the world, agricultural production could be better balanced with ecosystem and human health by prioritizing and implementing N removal tools like bioreactors at critical locations in the landscape. Tools to reduce nutrient pollution should be implemented at the spatial scale at which these pressures impact stream health, which is often the watershed-scale (Moerke & Lamberti, 2003). A holistic strategy that encompasses the rehabilitation of watershed-scale processes such as nutrient cycling, runoff regulation, erosion and sedimentation, as well as the provisioning of ecosystem services, has become a new paradigm for stream restoration (Palmer, Hondula & Koch, 2014). However, the broad implementation of BMPs and stream rehabilitation tools to address N are limited by land availability, sociopolitical acceptance, environmental consciousness, and financial constraints, amongst others, which favors the opportunistic implementation of remediation tools at smaller scales (Prokopy *et al.*, 2008).

Despite these constraints, opportunities can be found to combine farm-scale and watershed-scale information to prioritize and implement bioreactors at strategic locations to address excess nitrate-nitrogen loading. We contend that bioreactors may best improve stream ecology and ecosystem services when they are implemented at appropriate ecological spatial and temporal scales and are implemented as part of a larger waterway management plan.

By offering context-specific adaptability and targeting critical source areas (CSA) of pollution, such as tile drain outlets (Giri *et al.*, 2014), bioreactors are an appealing precision conservation tool that should be implemented synergistically as part of a nitrate-nitrogen remediation 'toolbox'. Precision conservation incorporates restoration approaches at the watershed-scale with strategically-placed mitigation tools at the farm-scale and recognizes the compatibility of economic and environmental goals in agricultural landscapes (Delgado & Berry, 2008). For example, (Tomer *et al.*, 2013) provide a framework for combining conservation technologies into agricultural watershed planning. Similarly, bioreactors could be implemented with two-stage channels to combine water quality, in-stream habitat, and biodiversity benefits to agricultural streams. We concur with (Christianson & Tyndall, 2011) that bioreactors are likely best suited for implementation within a N-mitigation toolbox to produce multi-scale synergies.

A variety of complementary land-based and stream-based management practices can reduce environmental losses of N in agricultural landscapes. Edge-of-field denitrification enhancement tools, including riparian fencing and vegetated buffers (Mayer *et al.*, 2007; Zhang *et al.*, 2010), constructed wetlands (Zedler, 2003; Hefting, van den Heuvel & Verhoeven, 2013), two-stage channels (Powell & Bouchard, 2010; Roley *et al.*, 2012), and denitrifying bioreactors (Schipper *et al.*, 2010b; Christianson *et al.*, 2012b) can remove N from agricultural streams. To provide a more thorough discussion and evaluation of bioreactors as stream rehabilitation tools, we encourage comparisons of bioreactor performance with other edge-of-field N remediation tools across a range of environmental conditions. Currently, we have not been able to find sufficient studies which have measured and compared these tools and have also measured ecological responses.

Compared to bioreactors, vegetated buffers and riparian wetlands that intercept agricultural runoff offer an expanded portfolio of ecosystem services, including the regulation of runoff, erosion, and climate support, as well as water storage, pollution remediation, carbon sequestering, biomass production, habitat creation, and enhanced biodiversity (Monaghan, de Klein & Muirhead, 2008; Christianson *et al.*, 2014). Therefore, although they enhance nutrient cycling and clean water, bioreactors may provide limited other ecosystem services, as compared to other edge-of-field N removal tools (Christianson *et al.*, 2014). However, these single benefits could be very relevant in specific agricultural settings where bioreactors may provide better primary vs. ancillary treatment options to remove excess N, such as the case for flat landscapes in the U.S. Midwest or in New Zealand dairy operations where water retention and treatment in the natural landscape are limited. Hence, the agricultural and landscape settings, as well as the range of ecological functions fulfilled by N removal tools need to be considered when selecting and siting appropriate N removal tools to rehabilitate stream health and ecosystem services of agricultural streams.

Analogous to bioreactors, in-stream experimental additions of bioavailable carbon can reduce N (Roberts, Mulholland & Hill, 2007). However, within the growing body of stream restoration literature, few studies have rigorously tested the effectiveness of stream-based measures to reduce N loading (Craig *et al.*, 2008). Typical stream restoration measures targeting N include re-connecting floodplains, re-meandering, re-connecting side channels, enhancing ground water to surface water connectivity, and adding large wood. These stream-based tools can enhance N removal through a variety of biogeochemical pathways, in addition to providing habitat for aquatic organisms and enhancing other ecosystem services. However, the highly variable performance of stream restorations to enhance N removal suggests that stream restoration and BMPs at their current practical scales of implementation are likely insufficient to generate 'measureable and meaningful water quality benefits' (Filoso & Palmer, 2011; Doyle & Shields, 2012). Furthermore, the application of these stream-based measures can be limited in agricultural landscapes because they may interfere with agricultural production and drainage provision. Thus, addressing N removal in agricultural streams necessitates implementing suites of complementary land-, tile drain-, and stream-based N removal tools to improve water quality, stream health, and ecosystem service provision.

Stream-based ecological monitoring of bioreactors

For bioreactors to more effectively contribute to stream health, we recommend that future evaluations of field-scale trials be conducted at ecologically-relevant timescales and further include the quantification of key environmental attributes that also underpin ecosystem functions and services (Table 2.1). Determining what suite of metrics best describes ecological 'health' varies widely by ecosystem and for the ecosystem services or restoration goals (Palmer & Febria, 2012). Assessing stream ecological functions often involves multiple spatial and temporal measurements, and significant differences in stream health sometimes develop five or more years after implementation. In the case of bioreactors, their optimum ecological impacts might only be detectable in situations where other edge-of-field and in-stream rehabilitation tools are already in place, such as riparian buffers and two-stage ditches, which target nutrients, fine sediment, and flashy stream flows in a synergistic fashion.

Therefore, considering the proximity of bioreactors relative to stream reaches with suitable streambed habitat will be important when evaluating their ecological impacts.

Above, we identified key knowledge gaps that would extend bioreactor performance into the realm of stream ecology. In turn, to fully understand the effects of bioreactors on stream health, monitoring should incorporate similar parameters involved in assessing bioreactor performance, together with short- and long-term ecosystem structure attributes, such as microbial activity or biomass, and macroinvertebrate taxa. For example, carbon lability and carbon source are indicators of ecosystem biogeochemical function, and they have been found to be negatively correlated with indicators of ecosystem structure, such as sensitive macroinvertebrate taxa (Parr *et al.*, 2016). Ecological evaluations should follow protocols similar to that of other restoration and management contexts (Table 2.1), whereby local climate and biophysical conditions are known, areas of bioreactor implementation are compared to upstream and downstream reaches with no bioreactors, and ecological indicators are measured on realistic timescales (i.e., multiple years).

Assessments of field-scale bioreactors should evaluate the impacts of bioreactor construction and performance on stream health indicators such as primary production, detritus processing, ecosystem metabolism, and invertebrate and fish assemblage structure and function. To assess bioreactors in a stream health context, we emphasize that projects should be implemented at relevant ecological scales (e.g., the stream network and watershed scale) and evaluated on ecologically-meaningful temporal scales (e.g., following key disturbances and 5 - 10 years post installation). Using a data-driven adaptive management approach, N remediation schemes can be scaled-up accordingly to incorporate additional ecological health impacts in their design and implementation.

Outlooks and conclusion

We propose that bioreactors tailored to farm-specific conditions and implemented strategically within a watershed might make significant contributions to improving water quality and ecosystem services. However, evidence of bioreactors' ability to improve stream health and ecosystem services is lacking. Therefore, it is imperative that edge-of-field tools to enhance N removal in agricultural streams be complemented by land-based nutrient management and other N removal tools at critical locations within farms and watersheds. Until better data on the N removal capacity of various biotechnologies and restoration tools are available, the implementation of bioreactors in different landscape contexts should be managed adaptively.

Table 2.1 Comparison of bioreactor performance criteria, stream health metrics, and stream ecosystem services. Ecosystem services are coded as follows: 1 fresh water provision, 2 water regulation (hydrological flows), 3 climate regulation, 4 water purification and waste treatment, 5 nutrient cycling, 6 recreational, and 7 aesthetic.

Bioreactor performance criteria	**Stream health metrics**			**References**	**Stream ecosystem services**
	Response variables	**Monitoring frequency**	**Monitoring locations**		
Inflow rate	Hydrologic regime	Pre- and post-implementation, >5 years post-implementation	Control vs treatment reaches	Poff *et al.*, 1997; Roley *et al.*, 2014	1, 2
Temperature	Climate/in-stream thermal regime	Seasonally, annually	Control vs treatment reaches	Poff *et al.*, 1997; Poole & Berman, 2001	3
Hydraulic residence time	Habitat complexity	Pre- and post- implementation	Channelized vs treatment /meandering reaches	Opdyke, David & Rhoads, 2006; Roley *et al.*, 2012	2, 3, 4
Carbon source	Carbon-sources/processing	Seasonally, annually	Upstream, at & downstream of treatments	Groffman, 2012; Griffiths *et al.*, 2012	1, 4
Dissolved oxygen (DO)	DO mg/L, Biological oxygen demand (BOD), metabolism	Seasonally, annually; >5 years post-implementation	Upstream, at & downstream of treatments	McTammany, Benfield & Webster, 2007; Warrner *et al.*, 2009	1, 4
N-load from land & from bioreactor	N-load in the waterway	Range of loading events including event-based, seasonally, annually; >5 years post-implementation	Upstream, at & downstream of treatments; Control vs treatment reaches	Groffman, 2012; Roley *et al.*, 2012	1, 3, 4, 5
Durability/longevity	Fine sediment	Seasonally, annually; >5 years post-implementation	Upstream, at & downstream of treatments	Wilcock *et al.*, 2009; Richardson *et al.*, 2011	1, 4
Maintenance	*E. coli*	Monthly, seasonally, annually	Upstream, at & downstream of treatments	Tanner *et al.*, 2012	1, 4, 6
	Chlorophyll-a (algae)	Seasonally, annually	Upstream, at & downstream of treatments; Control vs treatment reaches	McTammany *et al.*, 2007; Brisbois *et al.*, 2008	1, 4, 6, 7
	Greenhouse gases	Pre- and post- implementation	Upstream, at & downstream of treatments; Control vs treatment reaches	Jenkins *et al.*, 2010	3, 5
	Biodiversity (invertebrates, fish)	Seasonally, annually; >5 years post-implementation	Upstream, at & downstream of treatments; Control vs treatment reaches	McTammany *et al.*, 2007; Brisbois *et al.*, 2008	4, 5, 6, 7

Plate 3. An agricultural, headwater, spring-source emerges from the pasture, with a view of Mount Hutt (2190 m asl), 80 kilometres west of Christchurch on the Canterbury Plains

Photo: Brandon C. Goeller

Chapter Three:

Springs drive downstream nitrate export from artificially-drained agricultural headwater catchments

Introduction

Increased nutrient loading caused by agricultural land-use intensification is a driver of global change and poses significant challenges for managing freshwater ecosystems around the world (Vörösmarty *et al.*, 2010; Glibert, 2017). Agricultural land-use practices for crop and stock production have increased nitrate-nitrogen (NO_3-N) loading in receiving waters, causing eutrophication, toxic algal blooms, altered food webs, nitrate toxicity in groundwater, and anoxic dead zones in receiving estuaries (Camargo & Alonso, 2006; Glibert, 2017). Nitrate is readily leached and transported from agricultural soils depending on fertilizer application rate and timing, tillage practices, cropping systems, annual rainfall, and any artificial drainage through subsurface tile drains and open tributary drains (Randall & Goss, 2008). While land-based nutrient reduction strategies have long been the focus of efforts to curb nutrient loss from agricultural landscapes (Conley *et al.*, 2009), edge-of-field, riparian, and in-stream rehabilitation approaches have also become established management practices to reduce downstream nutrient fluxes (Schipper *et al.*, 2010a; Faust *et al.*, 2017). An important step to managing downstream nitrate loss is characterizing the rapid contaminant transfer pathways (RTP) from critical source areas (CSAs), such as gullies, swales, or artificial drainage from tile and open tributary drains, which can contribute disproportionate amounts of nutrient export on farm- and catchment-scales (White *et al.*, 2009; Bouraoui & Grizzetti, 2014). In particular, improved understanding of the influences of events that increase catchment nitrate export and the relative contributions of RTPs is needed to better guide actions to manage and mitigate excess nitrate loading from agricultural landscapes.

Small agricultural waterways, including drainage ditches and drains, often form the headwaters of larger streams and rivers, and these are sources of nitrate to downstream catchments (Greenwood *et al.*, 2012; McDowell, Cox & Snelder, 2017). In many agricultural landscapes, artificial drainage is used to remove excess water from wet soils. Globally, about 33 % of croplands require drainage ditches, open drains, or subsurface tile drains to enable agricultural production (Smedema, Vlotman & Rycroft, 2004). In many regions, more than 80 % of catchments are influenced by subsurface drainage (Blann *et al.*, 2009). Because tile drains alter hydrologic flow paths and fluxes of solutes and nutrients to agricultural waterways (Tomer *et al.*, 2003; Kennedy *et al.*, 2012; Williams *et al.*, 2015b), they can potentially be significant RTPs. For example, although tile drains can reduce the loss of sediment, and sediment-bound nutrients and pathogens to streams, they increase the movement of water-soluble nitrate to stream networks (Skaggs *et al.*, 2012; King *et al.*, 2015; Williams *et al.*, 2015b). Tile drains also transport other agricultural contaminants, including dissolved reactive phosphorus, fine inorganic sediment, agrichemicals, and *E. coli* (Blann *et al.*, 2009). Furthermore, subsurface drainage networks act as transport control points of nitrate export (Bernhardt *et al.*, 2017), because they ‘short-circuit’ potential nitrate removal zones in riparian buffers and anaerobic groundwater (Kellogg *et al.*, 2005). Therefore, even when farmers adopt best management practices (BMPs), significant amounts of nitrate can be exported downstream because of the enhanced waterway connectivity and limited riparian and in-stream denitrification capacity in agricultural waterways (David *et al.*, 2010; Glibert, 2017).

Characterising the magnitude, seasonality, and specific sources of nitrate fluxes in artificially-drained agricultural headwaters is necessary to guide more effective nutrient management practices and waterway rehabilitation tools. The transport of nitrate from artificially-drained agricultural lands creates spatially and temporally variable fluxes of nitrate across the land and within waterways (Gentry *et al.*, 2009). Plot- and field-scale studies have quantified nitrate fluxes from edge-of-field sources such as tile drains and surface drains (Logan, Eckert & Beak, 1994; Jaynes *et al.*, 2001; Kladivko *et al.*, 2004), and much progress has been made in understanding how fluxes of nitrate in agricultural headwater catchments affect downstream water quality and ecological conditions (Royer *et al.*, 2004; Alexander *et al.*, 2007; Freeman, Pringle & Jackson, 2007). However, understanding the scale and connectivity of nitrate fluxes in agricultural catchments and addressing these with scale-suited nutrient mitigation tools poses a substantial management challenge (Tomer *et al.*, 2013; Giri *et al.*, 2014). For example, temporal and seasonal variation in tile drain discharge, nitrate concentrations, and nitrate fluxes can mirror that in receiving waterways, indicating clear hydrological connectivity between surface water and subsurface drainage (Kennedy *et al.*, 2012; King, Fausey & Williams, 2014; Williams *et al.*, 2015b). Therefore, characterising the drivers of nitrate flux from tile and open tributary drains, as well as their relative contributions to catchment nutrient flux, is critical to designing and implementing appropriate nitrate attenuation tools to target RTPs at farm- and catchment-scales.

Despite the recognition that tile and open drains can be important nutrient RTPs, few studies have attempted to quantify the contributions of these to catchment nutrient loads (Williams *et al.*, 2015b), and even fewer studies have evaluated both farm- and catchment-scale nitrate-nitrogen fluxes for multiple catchments over multiple years (Royer, David & Gentry, 2006). This could be due to the logistical challenges and uncertainties associated with estimating nutrient loads from small, artificially drained headwaters (Wang, Frankenberger & Kladivko, 2003; Yanai *et al.*, 2015), which often limits water quality monitoring programmes. In an eight-year study of two cropped agricultural catchments in Iowa, USA, Tomer et al. (2003) found that nitrate fluxes from tile drains varied with discharge, and that waterway nitrate concentrations were generally not diluted by increased flows, indicating strong groundwater nitrate contributions. Similarly, Williams et al. (2015b) concluded that tile drain nitrate concentrations and discharge were the primary factors influencing downstream nitrate fluxes from a cropped, agricultural, headwater catchment in Ohio, USA, over eight years. Hence, the contributions of tile and open tributary drains to nitrate export at catchment outlets might be expected to vary seasonally with groundwater levels and rainfall affecting seasonal base flows. However, Monaghan et al. (2016) investigated the flow pathways of nutrient fluxes on artificially drained pasture plots in Southland, New Zealand, over three years and found a strong influence of storm events and season on the delivery and transformation of nitrate, dissolved organic phosphorus, and sediment to agricultural headwaters. Furthermore, groundwater nitrate pollution poses significant management challenges in landscapes with high groundwater concentrations and in landscapes currently undergoing agricultural intensification (McCrackin, Harrison & Compton, 2015; van Grinsven *et al.*, 2015). Therefore, understanding the contributions of tile drains and open tributary drains compared to upstream spring or other sources, and how these scale-up is a critical knowledge gap in reconciling the farm- and catchment-scale dynamics of nitrate loss from agricultural headwaters.

We undertook one of the first studies to measure and compare farm- and catchment-scale sources of nitrate fluxes for multiple waterways over multiple years. We investigated the timing and delivery of nitrate loads from tile drains, open tributary drains, and along 1000-m headwater reaches in nine spring-fed, artificially-drained, agricultural catchments over four years as part of the Canterbury Waterway Rehabilitation Experiment (CAREX). Contributions of tile drains, open drains, and groundwater (i.e., springs and upwellings) to catchment nitrate fluxes were evaluated across a gradient of groundwater NO_3-N spanning < 1 to > 15 mg L^{-1} on the Canterbury Plains, South Island, New Zealand, accounting for the effects of season and year. Our research aimed to disentangle the drivers of downstream nitrate flux from agricultural headwaters, including: 1) the relative importance of wet seasons and years, and 2) the contributions of upstream springs compared to tile and open tributary drains. We predicted that (H1) catchments with high headwater spring water nitrate concentrations would have the highest nitrate loads at catchment outlets, independent of the catchment farming practices or artificial drainage intensity. Given the strong groundwater contributions to the spring flows that supply these headwaters, we also predicted that (H2) wet years and wet seasons would increase nitrate loads. Finally, we expected that (H3) tile and open drain inputs would increase nitrate flux at catchment outlets, even where substantial groundwater inputs enter the waterway network from springs. An improved understanding of the spatial and seasonal drivers of nutrient fluxes across the land, groundwater, and surface water will help inform management of excess nitrate export from agricultural landscapes.

Methods

Study sites

The Canterbury Plains, located on the east coast of the South Island, New Zealand, were formed by alluvial outwash from glaciers during the last ice age (Webb, 2008). Most of the region is covered by well-drained, sandy and loamy soils. Canterbury has a cool and dry climate with a mean annual temperature < 12 °C and receives annual rainfall of 681 – 895 mm (Macara, 2016). The Plains were formerly covered by wetlands and native forest, but the current land use is predominantly pastoral agriculture (Pawson & Holland, 2008). Similar to other flatland agricultural regions of the world (e.g., Midwestern United States of America, southeastern Canada, and northern Europe), extensive networks of open agricultural drains, ditches, and subsurface tile drains were created to convert wetland and wet soils to fields and pastures, and these now form the headwaters of many catchments in Canterbury (Winterbourn, 2008). Over the last two decades, many agricultural regions of New Zealand, particularly the Canterbury Plains, have experienced rapid intensification and conversion to dairy farming, which has replaced traditional low-intensity sheep farming and cropping. For example, there were approximately 1,250,000 dairy cows in Canterbury in 2015, marking a 57% increase from 2012 or an 83% increase from 1994 (Statistics NZ, 2015). Dairy expansion in New Zealand has been associated with problematic increases in nitrate loading in waterways (Scarsbrook & Melland, 2015; Scarsbrook *et al.*, 2016). On the Canterbury Plains, diffuse nitrate leaching from agricultural lands has elevated groundwater nitrate levels to above the maximum drinking water guideline value of 11.3 mg L^{-1} NO_3-N set by the World Health Organization (World Health Organization, 2017), and surface water nitrate-nitrogen concentrations frequently exceed the median 6.9 mg L^{-1} NO_3-N ‘bottom line’ established by New Zealand’s National Policy Statement for Freshwater Management (Ministry for the Environment, 2017). Thus, balancing agricultural production with water quality and freshwater ecosystem service provision poses substantial management challenges in this region (Ausseil *et al.*, 2013).

Nine agricultural headwater catchments were studied as part of CAREX (Figure S3.1). The waterways, typical of small agricultural waterways in lowland Canterbury, were chosen to span a nitrate-nitrogen gradient from < 1 to > 15 mg L^{-1} NO_3-N to capture the regional variation in shallow groundwater nitrate-nitrogen concentrations. These small agricultural drainage ditches were spring-fed agricultural waterways (mean wetted widths 1.2 – 2.5 m) with mean annual flows ranging from 0.02 – 0.23 m^3 s^{-1}, received negligible or no storm runoff, had varying degrees of surface and subsurface drainage intensity, and formed the headwaters of downstream catchments (Table 3.1). The catchments encompassed a variety of farm types (e.g., dairy, cropping, sheep, or beef; Table 3.1). All study waterways were fenced to exclude livestock, had vegetated riparian buffers 2 – 4 m wide containing grasses, gorse (*Ulex europaeus*), sedges (*Carex* spp.), flax (*Phormium* spp.), and toetoe (*Austroderia* spp.), and were part of ongoing waterway rehabilitation efforts as part of CAREX.

Table 3.1 Catchment characteristics for the nine spring-fed agricultural headwaters sampled on the Canterbury Plains, New Zealand. Letters are the coded catchment names, listed in alphabetical order. NZSC soil groups follow the New Zealand Soil Classification system. Drainage intensity refers to the density of inputs from open tributary drains and subsurface tile drains per km of waterway, and categories are as follows: open drains (≤ 3 per km = low, ≥ 4 per km = high) and subsurface tile drains (≤ 5 per km = low, ≥ 6 per km = high). Mean annual rainfall, mean discharge, and mean nitrate-nitrogen concentrations are averages for the four-year study period August 2013 – August 2017. Rainfall was measured daily, while discharge and nitrate-nitrogen were measured monthly.

Catchment	**Farm type**	**Catchment area (ha)**	**NZSC soil group**	**Drainage intensity (surface/subsurface)**	**Mean annual rainfall (mm)**	**Mean discharge (m^3 s^{-1})**	**Mean NO_3-N (mg L^{-1})**
BO	dairy	50	humic organic	low/high	581	0.03	13.8
GR	cropping	81	orthic gley	low/high	581	0.06	12.1
HC	cropping	120	firm brown	low/low	581	0.12	12.5
HR	cropping & sheep/beef	91	humic organic	high/low	566	0.02	0.2
MB	dairy	140	orthic gley	high/low	512	0.05	0.9
MD	dairy	450	orthic brown	low/high	751	0.23	0.7
PY	dairy & sheep/beef	60	humic organic	low/low	581	0.04	10.3
SS	beef & dairy	108	orthic gley	low/low	566	0.13	6.7
YM	dairy	160	firm brown	low/low	581	0.07	10.9

Estimating annual nitrate loads and fluxes

We measured nitrate-nitrogen concentrations and discharge at least monthly at the downstream end of 1000-m study reaches (henceforth catchment outlets) for the nine catchments over four years from August 2013 – August 2017. Sampling years encompassed the start of the austral spring to the end of winter. Measurements of nitrate-nitrogen concentration and discharge were made seasonally spring – autumn each sampling year at four locations along the 1000-m study reach and at all flowing tile and open drain outlets along the same reach. At each in-stream sampling location, we measured the wetted width, depth, and water velocity using a Flow-Mate 2000 (Marsh-McBirney, USA) in a single transect across the thalweg. We calculated waterway discharge (m^3 s^{-1}) using the area integration method (Gordon *et al.*, 2012). At tile and open tributary drain outlets, we measured the wetted width, depth, and water velocity, and we calculated discharge with the area integration method (Gordon *et al.*, 2012). Water height at the downstream end of the study reaches was recorded hourly with WT-HR stage height loggers (TruTrack, New Zealand), and daily rainfall data were downloaded from the NIWA CliFlo database for the corresponding weather station within 20 km of each catchment (NIWA, 2017). Water samples were taken from mid-channel or from flowing tile or open drain outlets, filtered through Whatman glass fibre fine (0.7 µm) filters in the field, transported on ice, and frozen within 24-hours of sample collection in acid-washed (5 % HCl) plastic bottles until analysis. Samples were analysed for nitrate-nitrogen on an Easychem Plus analyser (Systea, Italy) using the cadmium reduction method at a detection limit of 0.01 mg L^{-1} NO_3-N (Rice & Eaton, 2017).

We quantified nitrate-nitrogen export as seasonal and annual loads (NO_3-N tonnes 90 d^{-1} or tonnes 365 d^{-1}, respectively) and daily fluxes (NO_3-N kg d^{-1}) to characterise catchment groundwater and farm-scale influences from tile and open drains on downstream nitrate-nitrogen export. We accounted for potential sources of error in our annual catchment nitrate-nitrogen load estimates by calculating minimum and maximum annual load ranges, assuming ≤ 10 % NO_3-N concentration error and ≤ 8.5 % of sample discharge error (Harmel *et al.*, 2006; Yanai *et al.*, 2015). Nitrate-nitrogen loads were calculated using the period-weighted averaging method (Likens *et al.*, 1977). This approach is known to be sensitive to sampling frequency compared with other ratio-based, regression-based, or composite load estimation methods (Appling, Leon & McDowell, 2015; Aulenbach *et al.*, 2016). However, it was selected because of the weak nitrate-nitrogen and discharge correlations (R^2 = < 0.001 – 0.43), and the low variability of nitrate-nitrogen concentrations and discharge at catchment outlets, which made it most appropriate (Williams *et al.*, 2015d; Aulenbach *et al.*, 2016). Due to the difficulties sampling tile drains and their unpredictable hydrology, we did not calculate annual loads from tile drains and open drains. Nitrate-nitrogen fluxes (NO_3-N kg d^{-1}) were calculated by multiplying nitrate-nitrogen concentrations with sample discharges for catchment outlets, in-stream sampling locations, and tile and open tributary drains. Because of the very weak relationships of stage height and discharge at catchment outlets (R^2 = 0.09 – 0.68), due to macrophytes 'holding up' the water level at low flows, only sample discharge measurements were used to calculate loads and fluxes. We did not compare catchment or tile drain nitrate-nitrogen yields (NO_3-N kg ha^{-1} y^{-1}) in this study, due to large uncertainties in delineating the contributing catchment areas for groundwater and surface water in these artificially drained, spring-fed waterways.

Statistical analyses

Time series of daily rainfall (mm) and mean daily waterway stage height (mm) were plotted for each of the nine catchment outlets to evaluate patterns of rainfall and waterway stage height over time. Daily rainfall (mm), sample discharge (m^{-3} s^{-1}), sample nitrate-nitrogen concentrations (NO_3-N mg L^{-1}), and sample nitrate-nitrogen fluxes (NO_3-N kg d^{-1}) were summarized by plotting duration curves for catchment outlets. Examining the probability exceedance of nitrate-nitrogen concentrations and fluxes, an emerging tool to examine patterns in nutrient export, extends the concept of flow-duration curves used by hydrologists to characterize stream flow (Tomer *et al.*, 2003).

All data analyses were performed in R 3.2.4 (R Core Team, 2016). Relationships between daily rainfall (mm), waterway stage height (mm), sample discharge (m^{-3} s^{-1}), and nitrate-nitrogen concentration (NO_3-N mg L^{-1}) were tested using linear regression to elucidate hydrological drivers of nitrate-nitrogen loss using (lm) in base R (R Core Team, 2016). Levene tests for homogeneity of variances were used to examine the variability of discharge, nitrate-nitrogen concentrations, and nitrate-nitrogen fluxes around group medians for catchment outlets versus tile drains and open drains along 1000-m headwater reaches using the car package (Fox & Weisberg, 2011).

Variance components analysis (VCA) was conducted using repeatability estimation and variance decomposition by generalized linear mixed-effects models with the rptR package (Stoffel, Nakagawa & Schielzeth, 2017). Mixed effects models were analysed using the lme4 package (Bates *et al.*, 2015). VCA was used to partition the overall variance in seasonal nitrate-nitrogen load that was accounted for by random factors in our experimental design: catchment, year, season, and residual variation. This VCA tested H1 to determine the effects of catchment groundwater springs on seasonal nitrate-nitrogen loads. We calculated 95 % confidence intervals for each repeatability estimate using 1000 bootstrapped iterations.

To test H2, we evaluated differences in seasonal nitrate-nitrogen loads (NO_3-N tonnes 90 d^{-1}) from the outlets of nine agricultural headwater catchments for four years using repeated measures analysis of variance ANOVA in base R (R Core Team, 2016). ANOVA tested for changes in seasonal nitrate-nitrogen load (NO_3-N tonnes 90 d^{-1}), with year (n = 4) as a random factor, season (n = 16) as a fixed factor, and year nested within catchment (n = 9) as an error term. Model fits and the 95 % confidence intervals were extracted for each seasonal nitrate load with the effects package (Fox, 2003).

We tested the drivers of nitrate-nitrogen flux (NO_3-N kg d^{-1}) using VCA to partition the overall variance in nitrate-nitrogen fluxes at catchment outlets, and from tile drains and open tributary drains, respectively, due to the random factors: discharge (m^3 s^{-1}), nitrate-nitrogen concentration (NO_3-N mg L^{-1}), and residual variation. We also used VCA to test the proportion of variance in nitrate-nitrogen flux at catchment outlets (NO_3-N kg d^{-1}) due to the random factors: nitrate-nitrogen flux from groundwater upwellings 1000 m upstream of catchment outlets, summed tile drain and open drain fluxes 1-km upstream of catchment outlets, and residual variation. The 95 % confidence intervals were calculated for each VCA repeatability estimate using 1000 bootstrapped iterations with the effects package (Fox, 2003). To test H3, we used linear regression with the lm function in base R (R Core Team, 2016) to separately examine the influence of nitrate-nitrogen flux (NO_3-N kg d^{-1}) at waterway sources 1000 m upstream of catchment outlets compared to the summed tile and open drain nitrate-nitrogen fluxes (NO_3-N kg d^{-1}) on nitrate-nitrogen fluxes at catchment outlets (NO_3-N kg d^{-1}).

Results

Catchment hydrology and discharge

There was no significant relationship between local daily rainfall (mm) and discharge (m^3 s^{-1}) measured at catchment outlets (n = 58 – 72, R^2 = 0.002 – 0.15), or for tile drains (n = 8 – 10, R^2 = 0.002 – 0.66) or open drains (n = 8 – 11, R^2 = 0.016 – 0.09). Thus, local rainfall did not drive patterns in discharge in either tributary drains or mainstems of our waterways. During the study, August 2013 – August 2014 and August 2016 – August 2017 were relatively wet years at all nine catchments; however, very few rainfall events > 20 mm d^{-1} occurred during any season or year (Figure 3.1A). Hence, the majority of our sampling events occurred at seasonal base flows, capturing the predominant hydrology of these spring-fed waterways (Figure 3.1B). Discharge measured from tile and open drains did not mirror changes in discharge at catchment outlets (tile drain discharge: n = 9 – 25, R^2 = 0.001 – 0.60; open drain discharge: n = 8 – 16, R^2 = < 0.001 – 0.22). Also, the measured ranges of tile and open drain discharges were significantly less variable than discharges at catchment outlets across all but one catchment ($F_{1,64}$ = 2.1755, p = 0.1451). Overall, across catchments, waterway discharge ($m^3 s^{-1}$) was more strongly influenced by annual and seasonal flows from groundwater than local rainfall or contributions from tile and open drains.

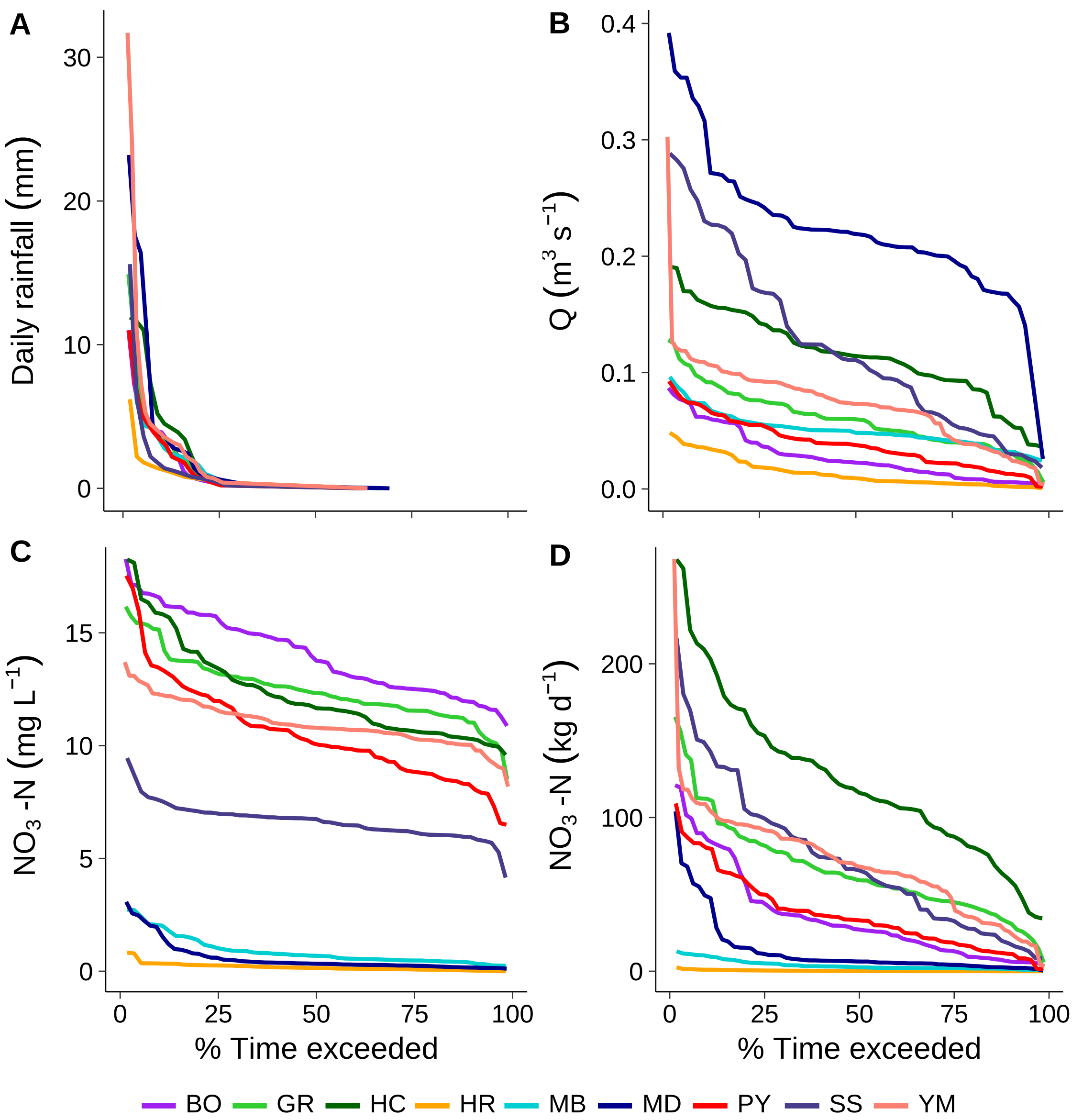

Figure 3.1 Duration curves summarizing hydrological measurements and water chemistry from August 2013 – August 2017 at nine agricultural headwater catchment outlets for (A) daily rainfall (mm d^{-1}), (B) stream discharge (m^3 s^{-1}), (C) nitrate concentrations (NO_3-N mg L^{-1}), and (D) nitrate fluxes (NO_3-N kg d^{-1}). Colours correspond to the coded catchment names. Curves for daily rainfall (A) do not extend to 100 % time exceeded due to the inclusion of days without rainfall.

Nitrate-nitrogen concentrations and loads

Mean annual nitrate-nitrogen concentrations observed across catchments ranged from < 1 to > 15 NO_3-N mg L^{-1}, with all catchments having consistent concentrations during the study (Figure 3.1C). Nitrate-nitrogen concentrations were not correlated with discharge at catchment outlets (n = 58 – 72, R^2 = < 0.001 – 0.43), tile drain outlets (n = 9 – 25, R^2 = 0.02 –

0.18), or open tributary drains (n = 8 – 16, R^2 = < 0.001 – 0.48), except for two open drains in catchments with the lowest nitrate-nitrogen concentrations (R^2 0.62, $F_{1,6} = 9.758$, $p < 0.05$; R^2 0.82, $F_{1,14} = 64.87$, $p < 0.001$). Tile and open drain nitrate-nitrogen concentrations varied within the ranges of corresponding nitrate-nitrogen concentrations observed at catchment outlets, except for one catchment, where the drains had a greater range in nitrate-nitrogen concentrations than the catchment outlet ($F_{1,109} = 34.441$, $p < 0.001$). On one rare sampling occasion with the highest nitrate-nitrogen concentrations, 52 and 55 mg L^{-1} NO_3-N were measured at two tile drain outlets, compared to 12 mg L^{-1} NO_3-N at the catchment outlet on the same day. Despite these rare events, overall, the patterns across four years and nine catchments indicated that the between-waterway differences in nitrate concentrations followed the between-catchment differences in regional shallow groundwater nitrate concentrations, with the potential for tile or open drains to contribute to downstream nitrate export.

Annual nitrate-nitrogen loads (NO_3-N tonnes 365 d^{-1}) differed markedly across the nine catchments, due to differences in stream size but not the catchments' predominant farming practices (Table 3.1; Table S3.1). Annual nitrate-nitrogen loads at catchment outlets ranged from < 1 to 72 tonnes NO_3-N 365 d^{-1}. Catchments with high nitrate-nitrogen concentrations also had high loads (H1; Figure 3.1). We observed consistent inter-annual load differences among catchments, with higher loads during wet years (i.e., August 2013 – August 2014 and August 2016 – August 2017) compared to lower loads during dry years (i.e., August 2014 – August 2015 and August 2015 – August 2016, Table S3.1). Two catchments had low annual nitrate-nitrogen loads (< 3 tonnes NO_3-N 365 d^{-1}), whereas four catchments had high annual nitrate-nitrogen loads exceeding 20 tonnes NO_3-N 365 d^{-1} (Table S3.1). Controlling for the effect of catchment on seasonal nitrate-nitrogen loads revealed an interaction between year and season significantly influenced loads at catchment outlets (Figure 3.2; Table 3.2). Wet years and wet seasons increased nitrate-nitrogen loads (H2; Figure 3.2). This was likely due to the influence of seasonal changes in waterway base flow that were exacerbated during wet or dry years. The highest seasonal nitrate-nitrogen loads (NO_3-N tonnes 90 d^{-1}) were observed in spring 2013 – autumn 2014 in three catchments; seasonal loads were lowest in two catchments in summer 2016 – autumn 2017 (Figure 3.2). However, over 75 % of the variation in seasonal nitrate-nitrogen loads was accounted for by catchment, whereas year and season explained < 1 % of variation in seasonal loads (Table 3.3). Thus, variations in nitrate-nitrogen loads were mostly driven by differences between catchments associated with the concentrations in upwelling groundwater nitrate-nitrogen (H1), and this strong influence of groundwater sources on catchment loads was manifested across all catchments during wet seasons and years (H2).

Table 3.2 Repeated measures ANOVA testing the influence of year and season on seasonal nitrate load (NO_3-N tonnes 90 d^{-1}) at nine agricultural headwater catchment outlets from August 2013 – August 2017. Year was treated as a random effect, season was treated as a fixed effect, and year was nested within catchment as an error term. NO_3-N load was measured in tonnes 90 d^{-1}. Bolded values show statistically significant results.

	df	**MS**	***F***	***P***
residuals: catchment	8	228103324		
year	3	38979912	5.85	**0.004**
residuals: catchment x year	24	6660333		
season	3	25641389	12.23	**<0.001**
year x season	9	6881871	3.28	**0.002**
residuals: catchment x year x season	96	2097178		

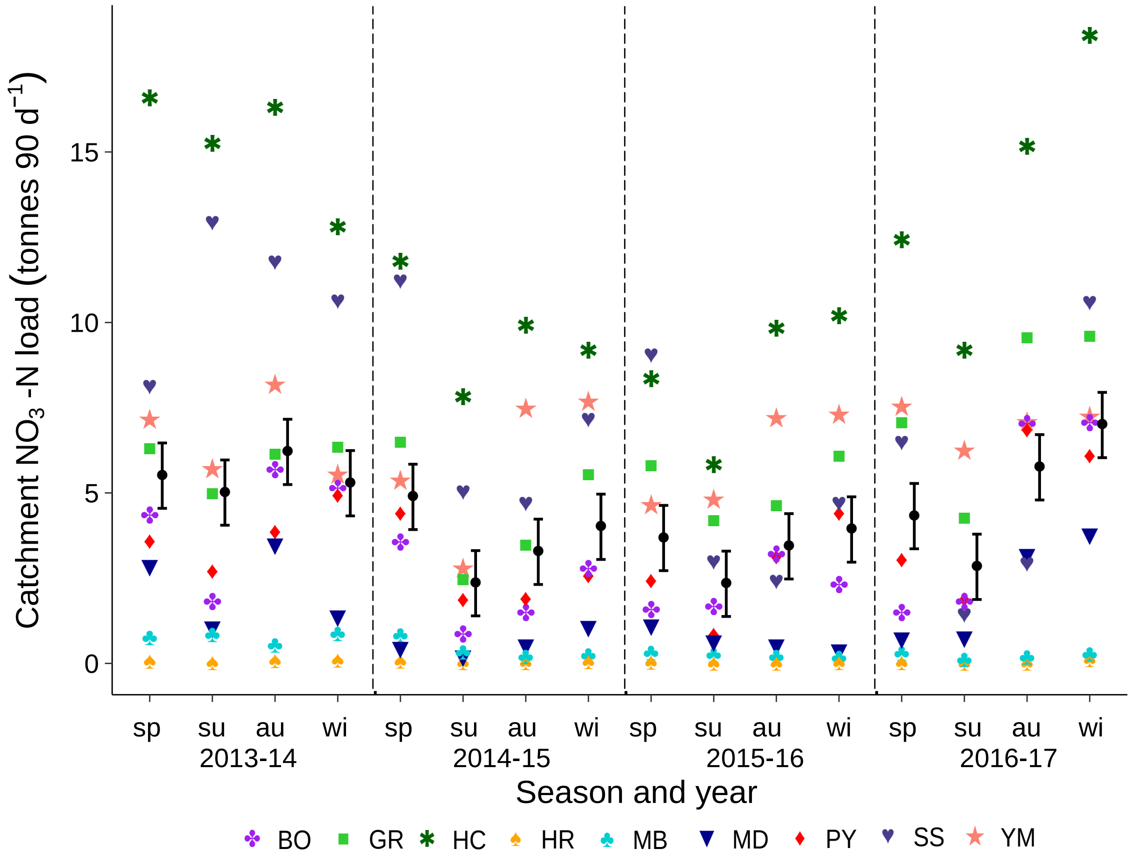

Figure 3.2 Seasonal nitrate loads (NO3-N tonnes 90 d^{-1}) measured at nine agricultural headwater catchments outlets from August 2013 – August 2017 showing measurements for individual catchments and model fits with 95 % confidence intervals. Coloured symbols represent each of the nine catchments, and black points and bars indicate model fits and 95 % confidence intervals from repeated measures ANOVA, respectively. Letters are the coded catchment names. Season abbreviations: spring (sp), summer (su), autumn (au), and winter (wi).

Scales and variability in nitrate-nitrogen flux

Nitrate-nitrogen fluxes at catchment outlets ranged from < 5 to > 100 kg NO_3-N d^{-1} (Figure 3.1D). Tile and open drain nitrate-nitrogen fluxes ranged from < 0.01 to > 50 kg NO_3-N d^{-1}. Thus, some of the agricultural catchments had very high fluxes, and the contributions of tile and open drains to catchment nitrate-nitrogen fluxes were quite substantial at times. Waterways with greater discharge (Figure 3.1B) generally also had higher fluxes of nitrate-nitrogen at catchments outlets (Figure 3.1D), irrespective of the magnitude of nitrate-nitrogen concentrations (Figure 3.1C). Variance components analysis revealed that discharge, nitrate-nitrogen concentration, and unexplained residual variation each explained ~33 % of variation in flux at catchment outlets (Table 3.3). However, for tile and open drains, discharge explained 98.6 % of variation in nitrate-nitrogen flux (Table 3.3). The greater contributions of discharge in explaining nitrate-nitrogen flux variation from tile and open drains, compared to catchment outlets, reflects the more flashy hydrology of these edge-of-field, farm-scale, sources of nitrate-nitrogen export compared to the steady, base-flow, contributions to catchments from groundwater springs that drive most of the discharge.

The flux of nitrate-nitrogen in the 1000 m upstream of catchment outlets, as well as the sum of all tile and open drain inputs of nitrate-nitrogen flux 1000 m upstream, were significantly correlated with flux at catchment outlets (in-stream flux: R^2 0.71, $F_{1,97} = 240.8$, $p < 0.001$, Figure 3.3A; tile and open drain fluxes: $R^2 = 0.15$, $F_{1,97} = 17.45$, $p < 0.001$, Figure 3.3B). Although edge-of-field nitrate-nitrogen fluxes from tile and open drains significantly influenced catchment fluxes (H3; $R^2 = 0.15$, $F_{1,97} = 17.45$, $p < 0.001$, Figure 3.3B), variance components analysis revealed that these farm-scale sources explained only 15 % of variation in fluxes at catchment outlets (Table 3.3). Fluxes from upstream springs and unexplained residual variation were also substantial, and these accounted for considerably more variation (46.2 % and 38.9 %, respectively) in catchment nitrate-nitrogen flux than tile and open drains (Table 3.3). Overall, these flux patterns indicate that although the majority of the variation in nitrate-nitrogen flux at catchment outlets (~60 %) was accounted for by in-stream and edge-of-field sources (i.e., tile and open drains), the remaining ~40 % of unexplained residual variation in flux further highlights the likely strong influence of regional groundwater to catchment nitrate-nitrogen export patterns.

Table 3.3 Variance components analysis (VCA) testing the relative contributions of catchment, year, season, and unexplained residual variation to seasonal nitrate loads (NO3-N tonnes 90 d^{-1}) at catchment outlets. The contributions of discharge ($m^3 s^{-1}$), nitrate concentration (NO3-N mg L^{-1}), and residuals of nitrate fluxes (NO3-N kg d^{-1}) to variation in nitrate fluxes (NO3-N kg d^{-1}) were examined at catchment outlets, and from tile drains (TD) and open drains (OD). Variance in catchment outlet nitrate flux (NO3-N kg d^{-1}) was also explained by upstream nitrate flux (NO3-N kg d^{-1}), summed tile drain and open drain nitrate fluxes (NO3-N kg d^{-1}), and residuals. 95% confidence intervals in VCA analysis were calculated for each repeatability estimate (R) using 1000 bootstrapped iterations.

Response	**Factor**	**R**	**95% CI**
Catchment NO_3-N	catchment	0.757	0.619-0.864
load (tonnes 90 d^{-1})	year	0.036	0.000-0.158
	season	<0.001	0.000-0.0949
	residual	0.207	0.125-0.284
Catchment NO_3-N	discharge	0.337	0.337-0.342
flux (kg d^{-1})	NO_3-N	0.326	0.321-0.327
	residual	0.337	0.335-0.338
TD & OD NO_3-N	discharge	0.986	0.973-0.994
flux (kg d^{-1})	NO_3-N	0.014	<0.001-0.0257
	residual	<0.001	<0.001-0.0183
Catchment NO_3-N	upstream flux	0.462	0.114-0.787
flux (kg d^{-1})	TD & OD flux	0.150	0.000-0.623
	residual	0.389	0.173-0.560

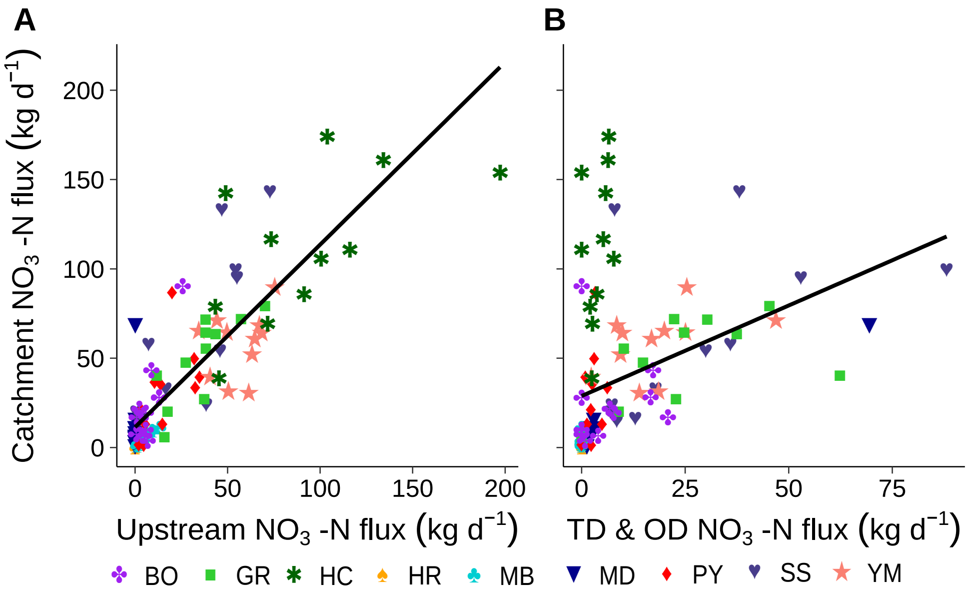

Figure3.3Linear regression predicting nitrate flux (NO_3-N kg d^{-1}) at catchment outlets from (A) the in-stream flux of NO_3-N 1000-m upstream and (B) the sum of all lateral drainage inputs of nitrate flux (NO_3-N kg d^{-1}) from tile drains (TD) and open drains (OD) along the same 1000 m reach. Coloured symbols represent samples taken during 11 seasonal sampling rounds from nine agricultural headwater catchments during August 2013 – August 2017. Letters are the coded catchment names. Lines indicate the overall model fit from linear regression.

Discussion

Worldwide, many agricultural landscapes are artificially drained, with the potential for groundwater inputs rather than surface runoff or stormflow to dominate waterway nitrate export (King *et al.*, 2014; Williams *et al.*, 2015b). Therefore, understanding the patterns and contributions from critical sources within the waterway network that exacerbate catchment nitrate loads is necessary to guide management actions to rehabilitate freshwater ecosystems (McCarty & Haggard, 2016). This study was the first to report multi-season, multi-year nitrate-nitrogen concentrations, loads, and fluxes from upstream sources, tile and open tributary drains, and catchment outlets across an agricultural region with spring-fed hydrology. Nitrate concentrations exceeded the World Health Organization human drinking water limit of 11.3 mg L^{-1} NO_3-N greater than 90 % of the time within four of the nine catchments and greater than 50 % of the time in another catchment. Nitrate-nitrogen loads were exported primarily during seasonal base flows during autumn and winter, especially during wet years. Partitioning the sources of variability in catchment nitrate fluxes revealed that ~60 % of variation was accounted for by fluxes from up-stream springs and the summed contributions from tile and open tributary drains (46.2 % and 15 %, respectively), with ~40 % of unexplained residual variation likely due to groundwater upwellings within the waterway. These variance partitioning results indicate that approximately 60 % of catchment nitrate loads could be mitigated with stream rehabilitation tools implemented along and within the stream network, while the remaining 40 % will need to be achieved through reductions from other sources, such as N inputs from land-use and groundwater. Identifying and comparing nutrient export from RTPs at the farm-scale is useful to elucidate the impacts of nutrient mitigation at catchment-scales (White *et al.*, 2009; Poudel *et al.*, 2013; Ghebremichael, Veith & Hamlett, 2013). Catchment groundwater springs and upwellings, edge-of-field contributions from tile and open drains, as well as the interactions of wet seasons and years were all important in understanding nitrate-nitrogen flux patterns across these catchments and provide information for targeting of management actions to attenuate nitrate-nitrogen from these sources. We discuss the details of these patterns below.

We measured annual catchment/downstream nitrate-nitrogen loads ranging from < 1 – 72 tonnes NO_3-N 365 d^{-1}, and the high loads corresponded to problematically-high nitrate-nitrogen losses from intensified agricultural land (Christianson & Harmel, 2015). Catchments with high spring water nitrate-nitrogen concentrations had the highest loads, consistent with our hypothesis (H1) that catchments with high spring or upstream nitrate-nitrogen concentrations would have high downstream loads. Given the difficulties in quantifying groundwater catchment boundaries and the seasonal and spatial changes in groundwater N inputs into our waterways, it may be misleading to estimate annual catchment nitrogen yields (kg NO_3-N ha^{-1} y^{-1}) using our data for these systems. Modelled nitrate-nitrogen leaching estimates from pastoral land-use in our region varied between < 2 to > 40 kg NO_3-N ha^{-1} y^{-1} (Dymond *et al.*, 2013), whereas modelled catchment nitrate-nitrogen yields for 1st and 2nd order streams were much lower < 1 – 4 kg NO_3-N ha^{-1} y^{-1} (McDowell *et al.*, 2017). However, we need to be circumspect about comparison of our measured loads with modelled nitrate-nitrogen losses for our region because of uncertainties due to sampling frequency, model selection, and model assumptions (Yanai *et al.*, 2015; Aulenbach *et al.*, 2016). Comparisons of our measured versus modelled nitrogen-losses is fraught because of inherent uncertainties in modelled estimates, especially since modelled results are usually applied at larger scales than field studies can characterise. It is likely that the modelled estimates from Dymond et al. (2013) and McDowell et al. (2017) did not include the prominent influence of groundwater upwellings and springs that drive the high catchment nitrate-nitrogen loads we measured. Similarly, our measured loads only pertain to the catchments measured and are complicated by groundwater inputs, which can complicate catchment N-load dynamics, both temporally and spatially. Therefore, we recommend that managing nutrient export at the catchment level will need to acknowledge farm-scale losses from land and the potential for substantial contributions from regional groundwater.

Seasonal groundwater influences on waterway base flows plays a key role in governing downstream nutrient export patterns (Mulholland & Hill, 1997). Field- and plot-scale studies of tile drain nutrient export indicate strong groundwater influences in driving nitrate-nitrogen export, particularly during storms, wet seasons, or wet years (Kennedy *et al.*, 2012; King *et al.*, 2014; Williams *et al.*, 2015b). We found that wet years and seasons increased loads (H2) across the entire gradient of nitrate-nitrogen concentrations and intensities of artificial drainage in the nine study catchments. These annual and seasonal patterns we observed are similar to those in other flatland agricultural headwaters on cattle farms (Eckard *et al.*, 2004; Monaghan *et al.*, 2016) and croplands (Randall & Mulla, 2001; Tomer *et al.*, 2003; King *et al.*, 2014) globally, where the majority of nitrate-nitrogen export occurs during wet conditions. For example, variations in preceding soil moisture conditions, ground water table elevation, and other factors affecting water drainage dynamics seasonally generally have a large influence on flow and nitrate-nitrogen export from artificially-drained agricultural headwaters (Kennedy *et al.*, 2012; Williams *et al.*, 2015d; Bauwe *et al.*, 2015). We observed the highest loads in late autumn and winter, which was likely related to elevated shallow groundwater levels at this time and the flushing of inorganic nitrogen stored in the soil over the preceding summer. Therefore, management actions to reduce nitrate inputs to waterways from groundwater and subsurface drainage, especially during wet periods, are recommended to reduce waterway N loads. Suitable options might include changes in irrigation practices or drainage water management (Williams, King & Fausey, 2015c; McDowell, 2017), in addition to stream rehabilitation tools that increase water retention and boost nutrient attenuation, such as two-stage channels, denitrification bioreactors, or constructed wetlands (Faust *et al.*, 2017).

Understanding the timing and drivers of headwater nitrate-nitrogen export is needed to inform farm-scale management and stream rehabilitation strategies to reduce downstream nutrient loss. For example, flashy hydrology within agricultural waterways can have a disproportionately high influence on downstream nitrate-nitrogen flux (e.g., > 50 % NO_3-N export occurred at extreme discharges ≥ 90^{th} percentile; Royer et al. 2006). We found that in-stream flux was primarily driven by discharge, such that waterways with greater discharge also had higher fluxes of nitrate-nitrogen at catchments outlets, with the magnitude of nitrate-nitrogen concentrations playing a minor role. Surprisingly, however, discharge at catchment outlets explained only 34 % of variation in nitrate-nitrogen flux at catchment outlets, with 33 % of variation explained by nitrate-nitrogen concentration and 34 % due to unexplained residual variation. In contrast, the relationships between discharge, nitrate-nitrogen concentration, and flux were very different for tile drains. We observed that individual tile drains had either steady, base flow, hydrology or were flowing very inconsistently over the four-year study duration. In a management context, this suggests that even potentially flashy sources of nitrate-nitrogen can behave predictably. Discharge explained 98 % of variation in nitrate-nitrogen flux in tile and open drains. The strong influence of discharge on tile drain nitrate-nitrogen fluxes is consistent with other studies showing links to antecedent soil moisture, water table elevation, and the depth and spacing of tile drains (Kennedy *et al.*, 2012; King *et al.*, 2014; Williams *et al.*, 2015b). Determining how changes in the hydrology and nutrient fluxes from the edge-of-field compared to within-waterway nitrate-nitrogen sources scale-up within catchments is necessary to direct management and stream rehabilitation actions to reduce downstream nitrate-nitrogen export.

We found that edge-of-field nitrate-nitrogen fluxes from tile and open tributary drains explained a significant amount of variability (15 %) in downstream fluxes, supporting our hypothesis that catchment nitrate-nitrogen fluxes would be influenced by these sources (H3). However, catchment-scale effects of groundwater inputs to waterways 1000-m upstream of catchment outlets had a stronger influence on nitrate-nitrogen flux at catchment outlets than did the sum of nitrate-nitrogen fluxes from tile drains and open drains 1000-m upstream of catchment outlets. Altogether, the majority of the variation in nitrate-nitrogen flux at catchment outlets (~60 %) was accounted for by edge-of-field and in-stream sources. The remaining ~40 % of unexplained residual variation in nitrate-nitrogen flux at catchment outlets in this study highlights the strong potential influence of groundwater on catchment nitrate-nitrogen fluxes. These findings differ from the majority of mass-balance studies of agricultural waterway nitrate-nitrogen export, where tile drains have more prominently influenced nitrate export (Royer *et al.*, 2006; Gentry *et al.*, 2009; Williams *et al.*, 2015b). For example, Royer et al. (2006) found that 55 % of the annual flux of nitrate-nitrogen at three catchment outlet in the Midwestern USA was due to base flow tile drain nitrate-nitrogen fluxes. Similarly, Williams et al. (2015b) reported that tile drains contributed between 44 – 82 % of nitrate-nitrogen export from a single catchment outlet in Ohio USA, with 44 % of annual discharge coming from surface runoff or groundwater. The strong influence of groundwater source catchments on nitrate-nitrogen flux within our study represents a different situation to these examples. Therefore, increasing groundwater nitrate-nitrogen loads in intensified agricultural landscapes and legacies of groundwater nitrate-nitrogen pollution (‘the load to come’; Schiel & Howard-Williams, 2016) represent significant catchment-scale concerns for managing downstream export (McCrackin *et al.*, 2015).

Small agricultural waterways with disproportionately high nutrient loads can play a significant role in influencing downstream water quality and ecological conditions (Freeman *et al.*, 2007; Pierce, Kröger & Pezeshki, 2012). Our results highlight that headwaters, including small agricultural drains, are just as important but likely more so for nitrate-nitrogen management than larger downstream waterways, due to the larger total length of headwaters in river networks (Meyer *et al.*, 2007). Therefore, in addition to farm nutrient pollution source controls to address N lost to groundwater and surface water, these small waterways should be targeted with stream rehabilitation tools to improve downstream conditions (Craig *et al.*, 2008; Thomas, 2014). Correspondingly, in a New Zealand-wide comparison of nutrient, sediment, and *E. coli* loads, McDowell et al. (2017) estimated that 77 % of mean NO_x-N loads to 4th – 8th order streams came from 1st and 2nd order agricultural headwaters. Therefore, we recommend that efforts to decrease nutrient loads downstream be targeted in headwater catchments, due to their significant contributions to downstream loads, as well as their potential to respond to stream rehabilitation actions (O'Brien *et al.*, 2017). Overall, our study indicates it is imperative that the contributions of nutrient loads from small agricultural headwaters be targeted with nitrate-nitrogen management options to improve water quality at larger spatial scales (Alexander *et al.*, 2007; Lassaletta *et al.*, 2010; McDowell *et al.*, 2017).

In conclusion, our results suggest that the influence of groundwater upwellings and the contributions of headwaters to downstream nitrate-nitrogen loads are substantial, and these headwater sources should be targeted with stream rehabilitation tools to improve downstream conditions. Groundwater contributions have been poorly accounted for in most nutrient load models and assumptions to date. However, we found across-catchment differences in upstream or spring water nitrate-nitrogen concentrations generally predicted differences in annual nitrate loads at catchment outlets, and loads were higher in wet seasons (autumn and winter) and wet years, reflecting strong groundwater influences. Nitrate-nitrogen loads varied most strongly across catchments, suggesting that the groundwater source of nitrate-nitrogen and its regional and seasonal variation were very important for predicting agricultural headwater nitrate-nitrogen concentrations, loads, and fluxes. Plans to limit catchment nitrate-nitrogen loads in this region should recognize that groundwater catchments can be more complex and not spatially aligned with surface water catchments; furthermore, operationalizing catchment-based nutrient attenuation strategies requires actionable knowledge of the locations and contributions of farm-scale sources to downstream nitrate-nitrogen loads (Jenkins, 2018). Although tile and open drains did not contribute as much to nitrate-nitrogen loads at catchment outlets as sources within the waterway 1000 m upstream, we propose that management actions targeted at these RTPs would help to attenuate downstream flux. Due to the high nitrate-nitrogen loads coming from groundwater in these spring-fed waterways, as well as the substantial fluxes delivered from subsurface tile drains, current nitrate-nitrogen waterway management and rehabilitation practices targeting waterway fencing are likely insufficient by themselves to reduce annual nitrate-nitrogen export from these catchments. Therefore, we recommend that local waterway nitrate-nitrogen management efforts should focus on intercepting the pathways of nitrate-nitrogen delivery (e.g. from edge-of-field RTPs like tile and open drains) and improving conditions to enhance nitrate uptake in riparian zones and within waterways (Newcomer Johnson *et al.*, 2016; Neilen *et al.*, 2017; O'Brien *et al.*, 2017). Substantial nitrate-nitrogen fluxes from tile and open tributary drains should be targeted for management at the farm-scale to complement catchment-scale and land-based nitrate attenuation measures.

Supplement to Chapter Three

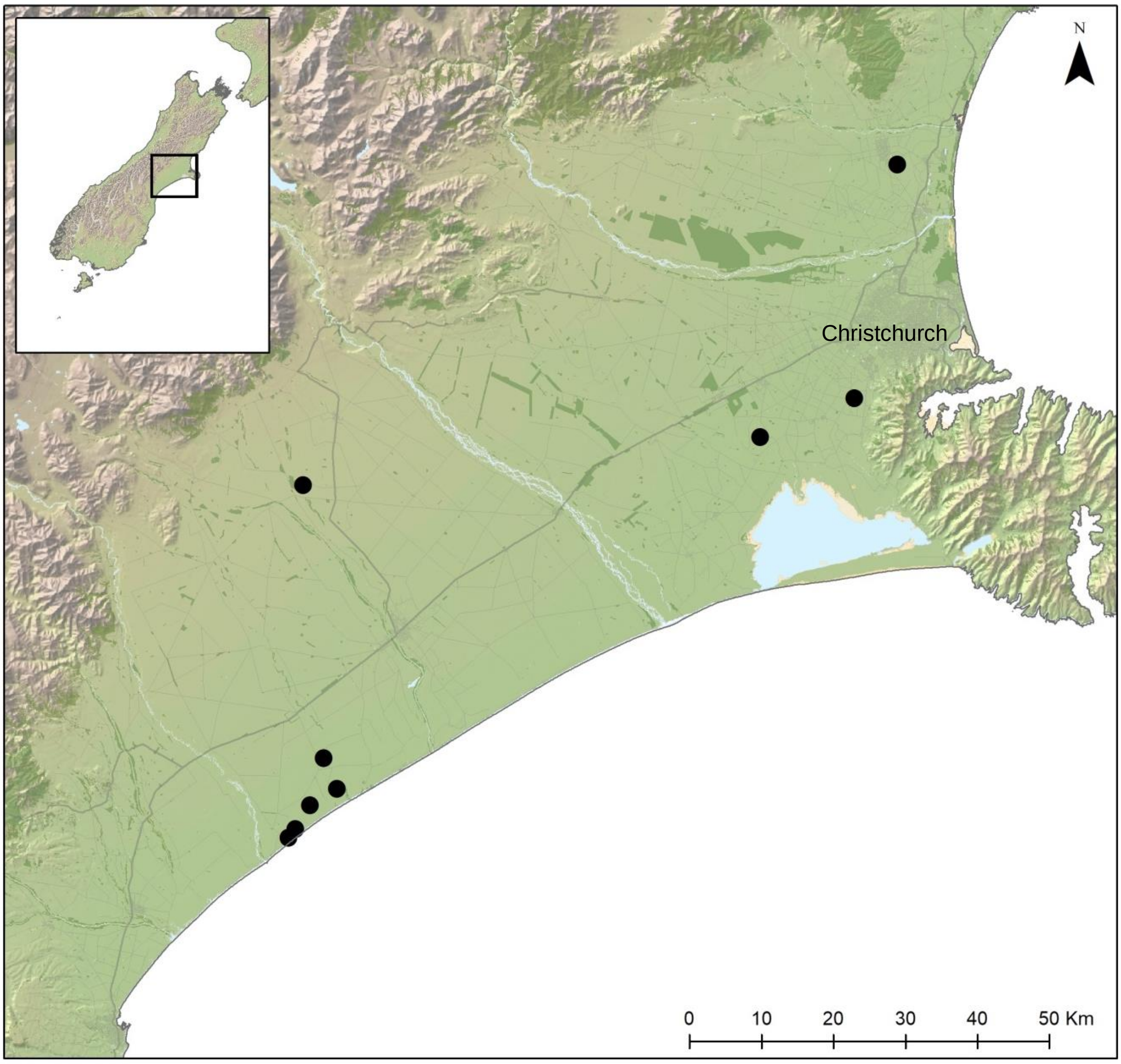

Figure S3.1 Locations of the nine spring-fed agricultural waterways (black circles) on the Canterbury Plains, South Island, New Zealand (inset), sampled from August 2013 – August 2017 as part of the Canterbury Waterway Rehabilitation Experiment (CAREX). Contours and brown shading indicate elevation; light green shading is pastoral land use, dark green shading is forest, and major rivers and lakes are light blue. Map prepared by Simon Coats.

Table S3.1 Annual nitrate mass loads (NO3-N tonnes 365 d-1) measured at nine agricultural headwater catchment outlets from August 2013 – August 2017. Letters are the coded catchment names, listed in alphabetical order. Load estimates are ranges calculated with ≤ 10% NO3-N (mg L-1) and ≤ 8.5% stream discharge (m3 s-1) measurement uncertainty.

Catchment	Year	NO_3-N load range (tonnes 365 d^{-1})
BO	2013-14	13.89-20.14
	2014-15	7.04-10.20
	2015-16	7.10-10.29
	2016-17	14.21-20.60
GR	2013-14	19.57-28.36
	2014-15	14.78-21.41
	2015-16	17.03-24.68
	2016-17	25.10-36.38
HC	2013-14	50.09-72.59
	2014-15	31.78-46.05
	2015-16	28.07-40.67
	2016-17	45.36-65.73
HR	2013-14	0.18 0.26
	2014-15	0.10-0.14
	2015-16	0.03-0.05
	2016-17	0.10-0.14
MB	2013-14	2.44-3.54
	2014-15	1.28-1.86
	2015-16	0.74-1.08
	2016-17	0.67-0.97
MD	2013-14	7.02-10.17
	2014-15	1.64-2.37
	2015-16	1.97-2.86
	2016-17	6.75-9.79
PY	2013-14	12.39-17.95
	2014-15	8.81-12.76
	2015-16	8.85-12.83
	2016-17	14.67-21.27
SS	2013-14	35.71-51.75
	2014-15	23.06-33.42
	2015-16	15.68-22.72
	2016-17	17.55-25.43
YM	2013-14	21.81-31.60
	2014-15	19.11-27.70
	2015-16	19.64-28.46
	2016-17	23.06-33.42

"Our tools are better than we are, and grow better faster than we do. They suffice to crack the atom, to command the tides, but they do not suffice for the oldest task in human history, to live on a piece of land without spoiling it."

Aldo Leopold (1991), 'Engineering and Conservation'

Plate 4. CAREX riparian rehabilitation with fencing, stream bank re-shaping and native vegetation to filter sediment, faecal bacteria, and nutrients from entering a headwater stream. Clockwise from top left, the photos show: 1) removal of a hedge blocking the waterway, 2) stream bank re-shaping, 3) riparian planting, and 4) growth of riparian plants three years post-rehabilitation

Photos: Hayley S. Devlin

Chapter Four:

Small-scale denitrifying woodchip bioreactors combined with riparian rehabilitation enhance agricultural waterway nitrate flux attenuation, but only at low flows

Introduction

Non-point source nutrient pollution from agricultural landscapes is a major cause of declining freshwater quality and impaired ecosystem functioning globally (Ansari *et al.*, 2011; Glibert, 2017). Small waterways and ditches (headwaters < 2 m wide, catchments < 10 km^2) that drain agricultural landscapes are often significant pathways for transporting excess nutrients to downstream catchments (Blann *et al.*, 2009; David *et al.*, 2010). Surprisingly, however, these agricultural headwaters are rarely targeted by environmental policy and stream water quality mitigation programs in the United States (Doyle & Shields, 2012), the European Union (Lassaletta *et al.*, 2010), or Australasia (McDowell *et al.*, 2017). Excess nutrients from these waterways can cause eutrophication, harmful algal blooms, hypoxia, toxicity, altered food webs, and dead zones that transcend farm boundaries (Diaz & Rosenberg, 2008; Breitburg *et al.*, 2009; Howarth *et al.*, 2011). Therefore, small agricultural waterways should be targeted for stream rehabilitation to attenuate downstream nutrient fluxes (Greenwood *et al.*, 2012; McDowell *et al.*, 2017). In particular, targeting rapid contaminant transfer pathways (RTP) from critical source areas (CSAs) that contribute disproportionately to nutrient input to agricultural headwaters is needed to complement land-based nutrient management (Di & Cameron, 2002; Kröger *et al.*, 2013; Tomer *et al.*, 2013).

Tools to reduce nitrate loss should seek to minimize the pathways of nutrient delivery and improve the conditions to enhance nutrient attenuation in riparian zones and within waterways (Newcomer Johnson *et al.*, 2016; Neilen *et al.*, 2017; O'Brien *et al.*, 2017). These small waterways are often channelized, decoupled from their floodplains, riparian wetlands, and forests, and have variable connectivity to soil water (Stutter *et al.*, 2018). They also receive groundwater nitrate from subsurface tile drains, open tributary drains, and riparian seeps (Blann *et al.*, 2009). In many catchments, nitrate inputs from groundwater and tributaries like subsurface tiles or open drains can be substantial (Chapter Three). While tile drains can help mitigate inputs of sediment loads and associated sediment-bound nutrients like phosphorus to waterways through reducing the potential for surface run-off, these buried networks of pipes and drains exacerbate the transport of nitrate, farming chemicals, and faecal bacteria to stream networks (Jamieson *et al.*, 2002; Blann *et al.*, 2009; Skaggs *et al.*, 2012). The transport of nitrate from tile drains to waterways is particularly problematic, since tile drains short-circuit nutrient removal sinks in the riparian zone and anaerobic groundwater (Jaynes & Isenhart, 2014). Overall, the consequences of the enhanced soil to waterway connectivity, as well as the lack of in-stream structures or pools to retain organic matter, result in small agricultural waterways that not only receive high nutrient loads, but also are often less efficient at removing nitrate via denitrification or assimilation by stream biota (Peterson *et al.*, 2001; Birgand *et al.*, 2007; Arango & Tank, 2008). Considering these factors alone, it is obvious a rehabilitation approach that targets these multiple inputs of nitrate is advantageous to nutrient mitigation and stream rehabilitation efforts.

Although nitrate loss mitigation tools are becoming prominent features of stream rehabilitation (Newcomer Johnson *et al.*, 2016; Faust *et al.*, 2017), all too often, these tools are not implemented in a complementary way that combines different tools across multiple spatial scales (Tomer *et al.*, 2013; Kröger *et al.*, 2015). A variety of nutrient attenuation tools can reduce nitrate loss in riparian zones and in-stream (Faust *et al.*, 2017), including: riparian fencing and vegetated buffers (Mayer *et al.*, 2007; Zhang *et al.*, 2010), constructed wetlands (Zedler, 2003; Hefting *et al.*, 2013), two-stage channels (Powell & Bouchard, 2010; Roley *et al.*, 2012), drainage water management (Ehmke, 2013; Kröger *et al.*, 2015), and denitrifying (woodchip) bioreactors (Schipper *et al.*, 2010b; Christianson *et al.*, 2012b). These tools can enhance nutrient removal along and within agricultural headwaters (Mander *et al.*, 2017; Lammers & Bledsoe, 2017), but, evidence is needed to show how implementing multiple tools in differing combinations and scales along and within the stream network may maximise their benefits to downstream water quality and ecosystem functioning (Kröger *et al.*, 2015). Waterway fencing to exclude livestock access and riparian planting are widely recognised as best management practices (BMPs) (McKergow, Matheson & Quinn, 2016; Mander *et al.*, 2017). Although riparian buffers can provide a broader suite of ecosystem services compared to other nitrate attenuation tools (Stutter, Chardon & Kronvang, 2012; Christianson *et al.*, 2014), riparian planting may offer limited treatment for nitrate from tile drains or riparian seeps (Mayer *et al.*, 2007; Jaynes & Isenhart, 2014). Also, in catchments with sparse or highly variable riparian groundwater contact due to over-steepened stream banks, or with limited riparian vegetation cover or insufficient organic matter stocks, riparian nitrate removal via denitrification can be limited (Webster, Groffman & Cadenasso, 2018). Furthermore, Weller and Baker (2014) concluded that even if agricultural waterways had complete riparian buffers, in intensified agricultural regions with high soil water and groundwater nitrate, substantial amounts of nitrate would still likely pass through riparian zones and streams. Therefore, mounting evidence suggests that implementing combinations of different nutrient mitigation practices and tools may be necessary to enhance opportunities for nitrate attenuation along the stream corridor, yet these have rarely been trialled at scales larger than single fields or experimental plots.

Denitrifying (woodchip) bioreactors can augment the nitrate losses expected from denitrification in riparian buffers and wetlands, and they can be implemented alongside land-based, riparian, and stream-based nutrient removal tools (Christianson *et al.*, 2012a). Bioreactors are generally woodchip-filled trenches designed to intercept nitrate-laden agricultural drainage water. The woodchips serve as a carbon supply that promotes anaerobic conditions and fuels heterotrophic denitrification reactions (Chapter Two). The scalability of bioreactors to enhance nitrate load removal under a variety of flow and nitrate loading scenarios, and the additional benefit of not removing land from agricultural production, makes them an attractive nitrate loss mitigation tool to farmers and catchment managers (Christianson *et al.*, 2012a). Field-scale bioreactors remove nitrate at an efficiency range from 1 – 98 % (Christianson *et al.*, 2012b; David *et al.*, 2015; Hartz *et al.*, 2017; Hassanpour *et al.*, 2017). Surprisingly, however, few studies have evaluated or compared the follow-on effects of bioreactor performance on in-stream water quality or ecosystem functioning in real agricultural settings (Christianson *et al.*, 2014; Weigelhofer & Hein, 2015; Goeller *et al.*, 2016). Rather, ecological evaluations of bioreactor performance are sparse, or primarily focus on the potential of bioreactors to contribute to pollution swapping via the creation of greenhouse gases (GHG) and other undesirable waste products associated with strong and variable bioreactor redox gradients (Fenton *et al.*, 2014, 2016; Weigelhofer & Hein, 2015). Although the engineering and biochemical design variables that control bioreactor performance are well documented (Addy *et al.*, 2016), studies of the linkages between bioreactor performance and changes to in-stream water quality or other ecological functions are rare. Such knowledge is required to understand the true water quality and ecological benefits of denitrifying bioreactors, and guide their implementation (Goeller et al., 2016).

We evaluated the performance of bioreactors implemented within a multi-year, multi-scale stream rehabilitation programme – the Canterbury Waterway Rehabilitation Experiment

(CAREX) – that involved waterway fencing to exclude livestock, stream bank reshaping, riparian planting measures, and a suite of in-stream restoration tools that addressed multiple in-stream stressors. In this study, we specifically aimed to investigate how the performance of three small (< 30 m^3) woodchip denitrification bioreactors in conjunction with other tools influenced net downstream changes in waterway nitrate fluxes. We hypothesized that (H1) paired bioreactors and riparian rehabilitation measures would improve net depletions in nitrate fluxes (kg NO_3-N d^{-1}) in a rehabilitated waterway compared to a control waterway with little stream rehabilitation. The small-scale bioreactors were designed to be highly cost effective and fit-for-purpose within farming practices and waterway management. We predicted that (H2) multiple bioreactors applied along a waterway would reduce nitrate export from edge-of-field sources to the receiving waterway. The redox gradients promoted within bioreactors may also be responsible for releasing other unwanted by-products such GHG, leading to 'pollution swapping' (Fenton *et al.*, 2014; Weigelhofer & Hein, 2015). To examine the pollution swapping potential of bioreactors, we compared the GHG fluxes from bioreactors, pasture soils, and riparian plantings with native vegetation. We hypothesized (H3) that greenhouse gas fluxes from bioreactors would be comparable to emissions from farm pastures and riparian zones. Our study provides one of the first assessments of bioreactors in a paired implementation trial for catchment nutrient attenuation.

Methods

Study site and local context

The study was conducted on the Canterbury Plains, on the east coast of the South Island, New Zealand. Originally formed from Quaternary gravel outwash deposits, the Canterbury Plains represent the largest area of flat land in New Zealand. Although once covered by wetlands and native forest, since European settlement in the 1850's, the land has been used primarily for pastoral agriculture (Pawson & Holland, 2008) and recently grown into an important centre for dairy farming (Livestock Improvement Corporation & Dairy NZ, 2016). The climate is cool and dry with a mean annual temperature < 12 °C and low annual rainfall of 681 – 895 mm (Macara, 2016). Although very productive, the light, stony soils of the Canterbury Plains have limited water holding capacity (Webb, 2008); hence, nitrate leaching from intensified farming is a major problem for groundwater and surface water quality (Carrick *et al.*, 2013; Scarsbrook *et al.*, 2016). Canterbury's agricultural practices are highly intensified, with limited natural water retention and treatment options in the riparian zone or within waterways, due to land clearance and drainage (Pierce *et al.*, 2012). Networks of agricultural drains, ditches, and subsurface tile drains form the headwaters of many catchments in lowland Canterbury (Winterbourn, 2008). These waterways were negatively impacted by nuisance aquatic weeds, deposited fine sediments, high nitrate-nitrogen levels above the World Health Organization human drinking water guideline of 11.3 mg L^{-1} NO_3-N (World Health Organization, 2017), and had depauperate freshwater communities (Burdon *et al.*, 2013). To mitigate the adverse environmental impacts of intensified agriculture, regional environmental plans aim to reduce nutrient and GHG losses at the farm boundary, in addition to rehabilitating stream water quality and biodiversity (Canterbury Mayoral Forum, 2009).

Riparian plantings, stream bank re-shaping, and bioreactor construction

We studied two 1000-m agricultural headwater reaches: a control waterway (two-letter catchment code: GR) with little riparian rehabilitation and a treatment waterway (YM) with rehabilitation added. The waterways were located 10 km apart in a region with orthic gley and firm brown soils. Both waterways were spring-fed agricultural headwater drainage ditches < 2 m wetted width (Figure 4.1). The control waterway drained a cropping and sheep farm (81 ha with peas and *Brassica* spp.), and the treatment waterway drained a dairy farm

(160 ha with 3.5 cows ha^{-1}), but both contained high nitrate levels > 10 mg L^{-1} NO_3-N. The streambeds in both waterways consisted predominantly of gravel, sand, and fine sediment < 2 mm and experienced seasonal build-up of emergent weedy macrophyte species monkey musk (*Erythrante guttata)* and watercress (*Nasturtium microphyllum*) from spring to autumn. The control waterway intercepted approximately a dozen tile drains along the 1000-m study reach, but the majority of these tiles were derelict or not flowing. The 1000-m study reach in the treatment waterway intercepted two tile drains and two open tributary drains, which had permanent flows from them. To inform the design of nutrient rehabilitation tools at these scales, we collected two-years of baseline water quality data to characterize the nitrate fluxes from tile and open tributary drains as part of CAREX (Chapter Three).

The control farm waterway was fenced along its entire length before 2013 to exclude sheep access in a 2 – 4 m-wide buffer. The streambanks in the control waterway were over-steepened from annual, mechanical clearance of emergent weedy macrophytes, with accumulations of excavated sand and gravel piled 1 – 2 m-high along both sides of the main channel. The narrow (less than 4 m-wide) riparian buffer contained pasture grasses and weeds, with no shrubs or shading along the waterway (Figure 4.1B).

For the treatment farm, initial nutrient loss actions were implemented when the farm was converted from cropping and sheep farming to dairying in 2008. This first phase involved fencing off the main headwater drainage channel to exclude livestock access. A 2-m wide buffer strip of grass and native vegetation, including sedges (*Carex* spp.), flax (*Phormium* spp.), and toetoe (*Austroderia* spp.), was planted along 3 km of the waterway. The second phase of nutrient retention measures from October 2015 – May 2016 implemented bioreactors, stream bank re-shaping to reduce sediment inputs from bank erosion due to over-steepened banks, and additional riparian plantings.

In October 2015 (austral spring), three different edge-of-field bioreactors were excavated. One bioreactor was constructed to intercept a single 20-cm-diameter tile drain (bioreactor Y1) and two other bioreactors were designed to intercept two other riparian groundwater upwelling zones/wet-spots (bioreactors Y2 and Y3) (Table S4.1). Shallow trenches were excavated to 1.2 m and filled with 20 – 30 m^3 of untreated pine woodchips (12 – 25 mm diameter, 30% moisture content), covered with geotextile, and capped with 30 cm of excavated fill and topsoil (Table S4.1). Plastic PVC piezometers with fine mesh bottoms were buried 15 cm above the bottom of the bioreactors at the inflow, midpoint, and outflow locations for sampling. The bioreactors were unlined, due to the propensity of locally heavy soils to retain water and because in other regions with heavy soils, unlined bioreactors have been used before (Christianson *et al.*, 2012a). In general, bioreactor dimensions are often designed to remove between 50 – 80 % of the influent nitrate load. However, smaller bioreactors connected to individual tile drain outlets or other RTPs may provide targeted and cost-effective nitrate attenuation. Our bioreactors were co-designed with the farmers to align with their preferred practices (i.e., they did not obstruct agricultural ditch maintenance or create flood risks, took up minimal land or were located within existing riparian margins, and addressed RTPs of nitrate export). Livestock access around bioreactors was restricted by 2-m fenced buffers containing pasture grasses.

In April 2016, following bioreactor construction, stream banks were re-shaped with a gentle slope to reduce the likelihood of stream bank collapse, and the fences were set back an additional 2 m along 2 km of the waterway. Finally, in May 2016, the extended riparian buffer was planted with a 2 to 4-m wide strip of native vegetation to filter fine sediment, faecal bacteria, and sediment-bound nutrients from entering the waterway. The additional riparian planting consisted of 1 – 2 rows of sedges (*Carex* spp.) planted 1-m apart along the water's edge, with 1-2 rows interspersed with larger vegetation set further back, including native shrubs (*Coprosma* spp., *Pittosporum* spp), flax (*Phormium* spp.), cabbage palms (*Cordyline australis*), and grasses in between plantings (Figure 4.1A).

FIGURE 4.1 The downstream end of the 1000-m study reach in the treatment waterway (YM) and the control waterway (GR) pre-rehabilitation in 2015 (A) and the treatment waterway with stream bank re-shaping, riparian planting, and bioreactors, two-years post-rehabilitation (B). Photos were taken by Brandon C. Goeller and Angus R. McIntosh.

Evaluating changes in stream nitrate flux

We sampled the control and treatment waterways seasonally for two years before and after bioreactor installation from austral summer (January) 2014 – spring (October) 2017. To enable us to test how stream water quality changed along the 1000-m study reaches, we sampled five sites along our waterways: 2 m upstream and 2 m downstream of subsurface tile drain or bioreactor outlets while they were flowing, as well as at 0, 500, and 1000 m downstream along the reach. We measured water quality parameters (temperature, pH, specific conductivity, dissolved oxygen, and turbidity), and nutrients (nitrate-nitrogen; soluble reactive phosphorus, SRP; and dissolved organic carbon, DOC) in the waterway thalweg. Turbidity was measured from grab samples with a portable infrared light meter (Eutech, Singapore) at a detection limit of 0.01 NTU. All other water quality parameters were measured *in-situ* with mutli-probes (YSI, Yellow Springs, USA).

Water samples for nitrate-nitrogen and phosphate analysis were filtered through Whatman fine glass fibre (0.7 µm Millipore) filters in the field, transported on ice, and frozen in acid-washed (5% HCl) plastic bottles until analysis. Nitrate-nitrogen and SRP (phosphate) were analysed colorimetrically on an Easychem Plus analyser (Systea, Italy) at detection limits of 0.01 mg L^{-1} NO_3-N and 0.1 μg L^{-1} PO_4 (Rice & Eaton, 2017). Dissolved organic carbon samples were filtered with Whatman fine glass fibre (0.7 µm Millipore) filters into acid-washed (5% HCl) amber glass vials and transported on ice. Dissolved organic carbon samples were acidified to a pH of 2-3 with 100% HCl in the laboratory and stored at 4 °C until analysis within 2-3 months (US EPA, 2003). Dissolved organic carbon was measured by catalytic oxidation with the TC-IC method (Shimadzu, Japan) at a detection limit of 4 μg L^{-1}.

Following stream water quality and nutrient sampling at each sampling location, we measured the wetted width and depth in a single transect across the thalweg. We measured stream water velocity across this transect using a Flow-Mate 2000 (Marsh-McBirney, USA), and waterway discharge (m^3 s^{-1}) was calculated according to the area integration method (Gordon *et al.*, 2012). We calculated nitrate-nitrogen fluxes (kg NO_3-N d^{-1}) at each sampling location and sampling time by multiplying waterway discharge by nitrate-nitrogen concentration.

Evaluating bioreactor performance: nitrate removal and greenhouse gas production

Bioreactor performance was evaluated every 6 – 8 weeks for two years after installation. Water quality parameters and nutrients were measured at bioreactor inflows, inside piezometers, and at outflows (Figure S4.2). Bioreactor nitrate, SRP, and DOC samples were collected and processed the same way as waterway samples. Nitrate concentrations at the inlets of bioreactors and the time that it takes for the effluent to move to the outlets can vary, affecting the precision of estimated nitrate-nitrogen removal rates (Warneke *et al.*, 2011a). Therefore, we also sampled bioreactors in piezometers mid-way along their length. Prior to sampling bioreactors, the elevation of the shallow groundwater table was measured, and 2 – 3 sample volumes of approximately 200 – 300 mL each were purged from each piezometer (Freeze & Cherry, 1979). Water samples for nutrient analysis and turbidity measurements were extracted from piezometers using a peristaltic pump (Masterflex, Vernon Hills, USA). Other water quality parameters were measured *in-situ* with mutli-probes (YSI, Yellow Springs, USA).

To verify the dissociation of nitrate to nitrogen dioxide gas and the potential pollution swapping of greenhouse gases along the treatment waterway, we sampled GHG fluxes from soils overlying bioreactor Y1, the adjacent pasture, and the restored native riparian planting during summer 2017, 16-months after bioreactor construction. We assumed that any increases in GHG from the bioreactors should be evident in the soil emissions above them. Gas samples were collected from soils overlying these sources in 1.5-L static PVC chambers which accumulated gas over 20 – 40 minutes. The static chamber trace gas measurement protocol was based on Baker et al. (2003). Samples of 250 mL gas volume were extracted with a syringe and stored in Tedlar bags (CEL Scientific, California, USA). Samples of 250 mL of ambient air were taken every 30 minutes from two metres height into the wind using syringes to inject the air into Tedlar bags. All GHG sampling occurred during late morning to minimise potential GHG flux variation due to diurnal fluctuations. The dry gas concentrations for CO_2 and N_2O were analysed within 12 hours of sample collection using cavity ring down spectroscopy (Picarro G2508, USA) at detection limits of 380 – 5000 mg L^{-1} and 0.3 – 400 mg L^{-1}, respectively. Soil gas fluxes of CO_2-C (mg C m^{-2} h^{-1}) and N_2O-N (μg N m^2 h^{-1}) were calculated by the change in gas concentration in the chamber headspace and using the molecular weight of the key element (Weissert, Salmond & Schwendenmann, 2016).

Measuring bioreactor hydraulic residence time and nitrate removal

We measured basic bioreactor hydrologic variables, including hydraulic residence time (HRT) and wetted volume. However, because our study aims were to investigate the overall effects of bioreactors, we did not conduct extensive groundwater monitoring to disentangle complex groundwater-surface water interactions or evaluate potential intra-bioreactor heterogeneity in flow (Ghane, Fausey & Brown, 2014; Jaynes *et al.*, 2016). Nitrate-nitrogen removal rates (g N m^{-3} d^{-1}) were calculated for the tile drain bioreactor Y1 as the change in nitrate concentration (g N m^{-3}) from the inlet to the outlet divided by HRT (time in d) (Warneke *et al.*, 2011a). Nitrate removal efficiency was calculated as the percentage of nitrate removed in the bioreactor from the inflow to the outflow. Since the highest nutrient export from agricultural RTPs often occurs at peak discharges, especially during wet seasons (Christianson & Harmel, 2015; Christianson *et al.*, 2016; Williams, King & Fausey, 2017), at least two peak flow events were sampled per year to determine bioreactor nutrient export during high discharge.

Water-level measurements in bioreactors were used to calculate the wetted, active bioreactor volume (m^3) on each sampling occasion. We calculated HRT (h) as the product of the active bioreactor volume and woodchip porosity divided by the measured discharge (Christianson *et al.*, 2012b). We calculated an average porosity value of 0.6 based on porosity values reported in other bioreactor studies (Van Driel, Robertson & Merkley, 2006; Chun *et al.*, 2009; Christianson *et al.*, 2010; Cameron & Schipper, 2010a). For wet-spot bioreactors Y2 and Y3, reference water-level measurements were made in piezometers in pastures and at the edge-of-field 2 m upgradient and downgradient of bioreactor flowpaths to estimate the hydraulic gradient. Because Y2 and Y3 bioreactor flowpaths intercepted soil and woodchips, we estimated a weighted hydraulic conductivity, taking into account the permeability of both media. We calculated an average hydraulic conductivity value of 7820 m d^{-1} for a 100% woodchip mixture based on a review of the literature (Robertson & Merkley, 2009; Christianson *et al.*, 2010; Cameron & Schipper, 2010b); for soils surrounding the bioreactors, we used a reference soil hydraulic conductivity value of 0.12 m d^{-1} for a loamy, moderately slow-draining soil.

Water height from the tile drain bioreactor Y1 was recorded at 15-min intervals using stage height loggers (TruTrack, New Zealand) in a small v-notch weir. We used stage-height and discharge relationships from the v-notch weir to calculate bioreactor discharge during the time of sampling (Gordon *et al.*, 2012). We assumed that the discharge of Y1 measured at the bioreactor outflow was equivalent to the discharge into the bioreactor inlet, and that leakage into or out of the bioreactor was minimal. Discharges measured from the v-notch weir (Y1) or estimated using the parabolic form of Darcy's law (Y2 and Y3) (Freeze & Cherry, 1979) were used to calculate bioreactor HRT.

Statistical analyses

A goal of our analysis (H1) was to test for changes in the net upstream to downstream waterway N fluxes along the 1000-m study reaches between two time periods in both the treatment and control waterways. In these spring-fed waterways, seasonal and annual groundwater inputs are important for catchment discharge and nitrate-nitrogen fluxes (Chapter Three). Because surface runoff may also be an important part of catchment hydrology, we tested relationships between daily rainfall (mm) and waterway discharge (m^{-3} s^{-1}) at the downstream ends of the 1000-m reaches from January 2014 – October 2017 using linear regression with the lm function in R (R Core Team, 2016). Also, waterway discharge, and therefore reach hydrological patterns, fluctuated seasonally with macrophyte growth and surface water abstraction for irrigation. For example, macrophyte growth 'holds up' water levels during summer periods of low flow, while surface water abstraction temporarily decreases water levels. Hence, discharge and nitrate-nitrogen fluxes were variable along reaches and over time, reflecting changes in these influences. Therefore, to detect changes in the upstream to downstream waterway N fluxes, we needed to characterise, contextualise, and summarise the key relationships between waterway hydrology and nitrate flux.

We used linear regression to evaluate longitudinal changes in waterway discharge (m^3 s^{-1}) and nitrate-nitrogen concentrations (NO_3-N mg L^{-1}) and nitrate-nitrogen fluxes (NO_3-N kg d^{-1}) at three or more sampling locations evenly spaced along 1000 m reaches on each sampling event (Figure 4.2). We used the slopes from these linear regressions with distance to standardise and summarise the prevailing waterway hydrological conditions. We expected that our multiple-tool rehabilitation approach would not change waterway discharge, but it would change the amount of nitrate entering a reach (Figure 4.2B). Because the upstream to downstream difference in nitrate flux at a given reach hydrology, measured by the slope of reach discharge versus distance, would not change without changes in nitrate concentrations, we used the slope of reach discharges versus distance from each sampling event as a covariate in our analysis (Figure 4.2).

To characterise the difference in nitrate fluxes from upstream (0 m) to downstream (1000 m) and standardise this response variable, we calculated log ratios (effect sizes) as: $\log_e$ NO_3-N flux in kg d^{-1} at the upstream end of the 1000-m reach divided by NO_3-N flux (kg d^{-1}) at the downstream end of the 1000-m reach. Calculating nitrate fluxes as log ratios was useful to summarise patterns in the data while providing ecologically meaningful and approximately normally-distributed responses (Shurin *et al.*, 2002).

We compared reach nitrate flux ratios with analysis of covariance (ANCOVA) using generalised linear models (glm) in R (R Core Team, 2016). Nitrate flux log ratios followed a non-linear distribution, were greater than zero, and were not whole numbers (Crawley, 2007), therefore, we constructed the ANCOVA using a glm with a quasi-poisson distribution using (glm) in R (R Core Team, 2016). The ANCOVA response variable was the nitrate flux ratio, the slope of reach discharge versus distance was the covariate, time (pre- or post-rehabilitation) was a fixed factor, and sampling events were replicates. We fitted the model separately for each waterway, and we removed the interaction of our covariate and time if it was non-significant with alpha set at 0.05. To reduce variation caused by rarely-occurring peak waterway discharge and to focus our analysis on the predominant base-flow conditions in these waterways, we excluded three storm-driven events from our analysis where nitrate fluxes were > 100 kg d^{-1}. In the treatment waterway, we analysed eight pre-restoration sampling events from January 2014 – October 2015 and nine post-restoration sampling events from October 2015 – October 2017. We excluded five post-rehabilitation sampling events from the ANCOVA because there were no equivalent pre-rehabilitation data that represented the same reach hydrology (our covariate). In the control waterway, we analysed seven sampling events in each of the pre- and post- sampling periods, which were representative of similar prevailing reach hydrological conditions. ANCOVA $\log_e$-

transformed model fits and 95 % confidence intervals were extracted for each waterway with the effects package and examined to interpret the statistical model outcomes (Fox, 2003).

Besides evaluating the overall impacts of the riparian rehabilitation programme on nitrate flux attenuation, we were also interested in elucidating the performance of our woodchip bioreactors. We analysed data from fifteen sampling events during the first two years of tile drain bioreactor Y1 operation from December 2015 – October 2017 to test whether the bioreactor removed nitrate from edge-of-field sources (H2). To examine changes in water quality and nutrients due to bioreactor performance, we evaluated relationships in the concentrations of dissolved oxygen, DOC, nitrate-nitrogen, and SRP from the inflow to the outflow of bioreactor Y1 using linear regression against length in m. To determine what influenced bioreactor nitrate removal performance, we used partial regression with (lm) in R to separately examine the influence of HRT (h), influent water nitrate-nitrogen concentrations (NO_3-N mg L^{-1}), and influent water temperature on nitrate removal efficiency (%) using data for all three bioreactors (R Core Team, 2016). We did not sample during or recently after rainfall to avoid problems with dilution (Van Driel *et al.*, 2006) and likely low uptake during high flow (Woli *et al.*, 2010). On several sampling occasions, water ponding above the bioreactor caused dilution of tile drain influent, so we excluded three sampling events impacted by this dilution from our analysis. The three sampling events that we excluded likely biased our bioreactor performance estimates towards higher N removal performance.

To evaluate the potential negative side effects of bioreactors due to pollution swapping (H3), we compared greenhouse gas fluxes of CO_2 (C mg m^2 h^{-1}) and N_2O (N μg m^2 h^{-1}) from local sources. We used Kruskal-Wallis rank sum tests to examine differences in greenhouse gas fluxes from the pasture, bioreactor Y1, and the native planting in the riparian zone of the treatment waterway. Because sample groups had unequal numbers of observations, we used

Dunn's post-hoc test of multiple comparisons to identify differences between groups (Zar, 2010). All data analyses were performed in R version 3.2.4 (R Core Team, 2016).

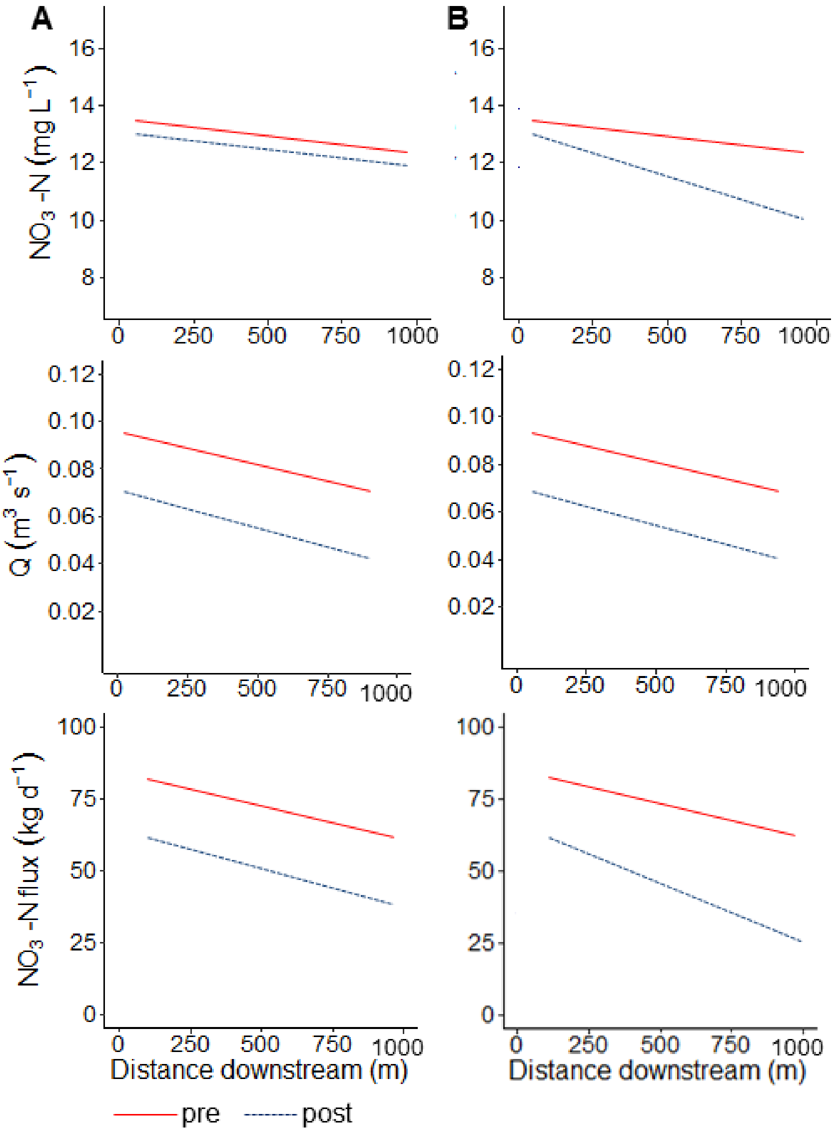

Figure 4.2 Hypothetical examples of upstream to downstream changes in treatment waterway nitrate-nitrogen concentrations, discharge, and nitrate-nitrogen fluxes from along the 1000-m treatment reach showing where the differences in upstream and downstream flux remained constant (A) or where there was likely a stream rehabilitation effect (B). In situations where there was no effect (A), the slopes of nitrate-nitrogen concentration, discharge, and nitrate-nitrogen flux are parallel. In situations where there was likely a rehabilitation effect (B), the slopes of nitrate-nitrogen concentrations and fluxes are not parallel, while discharge slopes remain parallel. Line colours and dashes indicate pre- (solid, red) or post-rehabilitation (dashed, blue) scenarios.

Results

Waterway hydrology, nutrient export patterns, and impacts of riparian rehabilitation

Our study encompassed two dry years in 2014 (pre-rehabilitation) and 2015 (post-rehabilitation), with 529 and 479 mm annual rainfall, respectively, as well as one relatively wet year in 2017 (post-rehabilitation) with 707 mm annual rainfall. Annual rainfall in 2016 was approximately equal to the 30-year average, with 591 mm. Overall, there were few large run-off events, and stream discharge at the downstream end of the 1000-m study waterways was not correlated with daily rainfall (mm) (treatment: $n = 22$, $R^2 < 0.01$, $p = 0.11$; control: $n= 14$, $R^2 = 0.03$, $p = 0.54$). Thus, our water quality sampling adequately characterised the prevailing nutrient export conditions for these spring-fed waterways. From upstream to downstream, mean waterway discharge ranged from 0.03 – 0.07 $m^3 s^{-1}$ (Table 4.1). In both waterways, mean nitrate-nitrogen concentrations were high (NO_3-N > 10 mg L^{-1}; Table 1), whereas mean SRP and DOC concentrations remained very low (PO_4 < 10 μg L^{-1}; DOC < 10 mg L^{-1}; Table 1). Mean nitrate fluxes from the downstream end of the study reaches averaged 58.2 and 52.9 kg NO_3-N d^{-1} for the rehabilitated and non-rehabilitated waterways, respectively, so nitrate fluxes were similar (Table 4.1).

Patterns in nitrate fluxes were variable over time, with both waterways switching between net gains and net losses of both nitrate-nitrogen and discharge along the 1000-m study reaches (Figure 4.3). These nitrate flux patterns were strongly influenced by changes in reach hydrology. In the control waterway (GR), nitrate flux ratios (effect sizes) decreased with increasing reach discharges (slope of reach discharge), indicating lower nitrate attenuation at greater reach discharges (ANCOVA, slope of reach discharge effect for control waterway: $F_{1,12} = 24.13$, $p < 0.001$; Figure 4.4). This relationship was consistent between pre- and post-treatment years (ANCOVA, time effect for control waterway: $F_{1,11} = 1.74$, $p = 0.21$; Figure 4.4).

In the rehabilitated, 'treatment' waterway (YM), the relationship of reach nitrate flux ratios (effect sizes) and the prevailing reach hydrology (slope of reach discharge) was different post-, compared to, pre-rehabilitation (time effect), indicated by a significant ANCOVA interaction between the slope of reach discharge and time ($F_{1,13} = 11.8$, $p < 0.01$; Figure 4.4). Downstream nitrate flux attenuation was greater under conditions of "losing" reach flow conditions (i.e., negative slopes of reach discharge) following rehabilitation, evidenced by no overlap of the 95% confidence intervals for the ANCOVA model fits for the pre- and post-rehabilitation sampling events at the lowest discharge slopes (Figure 4.4). However, as reach hydrology switched to "gaining" discharge down the reach, there were no differences in nitrate flux effect size ratios, indicated by overlapping 95 % confidence intervals for the ANCOVA model fits at higher discharge slopes (Figure 4.4). Overall, hydrological variability, assessed as changes in reach discharge, greatly influenced downstream nitrate fluxes, and, in particular, any attenuation in nitrate due to rehabilitation. Our results suggest that stream bank re-shaping and native riparian planting complemented by woodchip bioreactors enhanced nitrate flux attenuation, but only under the lowest flow conditions. They had no detectable effect under gaining reach hydrology.

Table 4.1. Mean stream discharge and nutrient concentrations (with 95 % confidence intervals) measured in waterways with (treatment) and without riparian rehabilitation (control) from January 2014 – October 2017. Distance downstream (m) refers to the 1000 m sample reaches.

Hydrology & nutrients	**YM – Treatment Distance downstream (m)**			**GR - Control Distance downstream (m)**		
	0	**500**	**1000**	**0**	**500**	**1000**
Discharge ($m^3 s^{-1}$)	0.06 (0.05 - 0.07)	0.06 (0.05 - 0.07)	0.06 (0.05 - 0.07)	0.03 (0.02 - 0.04)	0.05 (0.04 - 0.06)	0.05 (0.03 - 0.07)
NO_3-N ($mg L^{-1}$)	10.7 (10.3 - 11.1)	10.5 (9.8 - 11.2)	11.1 (10.5 - 11.6)	12.3 (11.3 - 13.3)	12.7 (11.9 - 13.5)	11.9 (11.1 - 12.9)
NO_3-N flux ($kg d^{-1}$)	55.1 (48.4 - 61.8)	56.8 (48.3 - 65.3)	58.2 (48.1 - 68.4)	37.3 (25.1 - 49.5)	56.8 (43.5 - 70.2)	52.9 (39.1 - 66.8)
PO_4 ($\mu g L^{-1}$)	3.3 (2.3 - 4.2)	3.6 (2.4 - 4.8)	5.3 (2.5 - 8.1)	4.8 (2.6 - 6.9)	1.7 (1.1 - 2.3)	2.6 (0.9 - 4.3)
DOC ($mg L^{-1}$)	2.8 (0.7 - 4.8)	4.6 (0.9 - 8.3)	7.6 (<0.1 - 21.6)	2.9 (1.2 - 5.8)	1.6 (1.2 - 5.8)	2.7 (1.2 – 5.9)

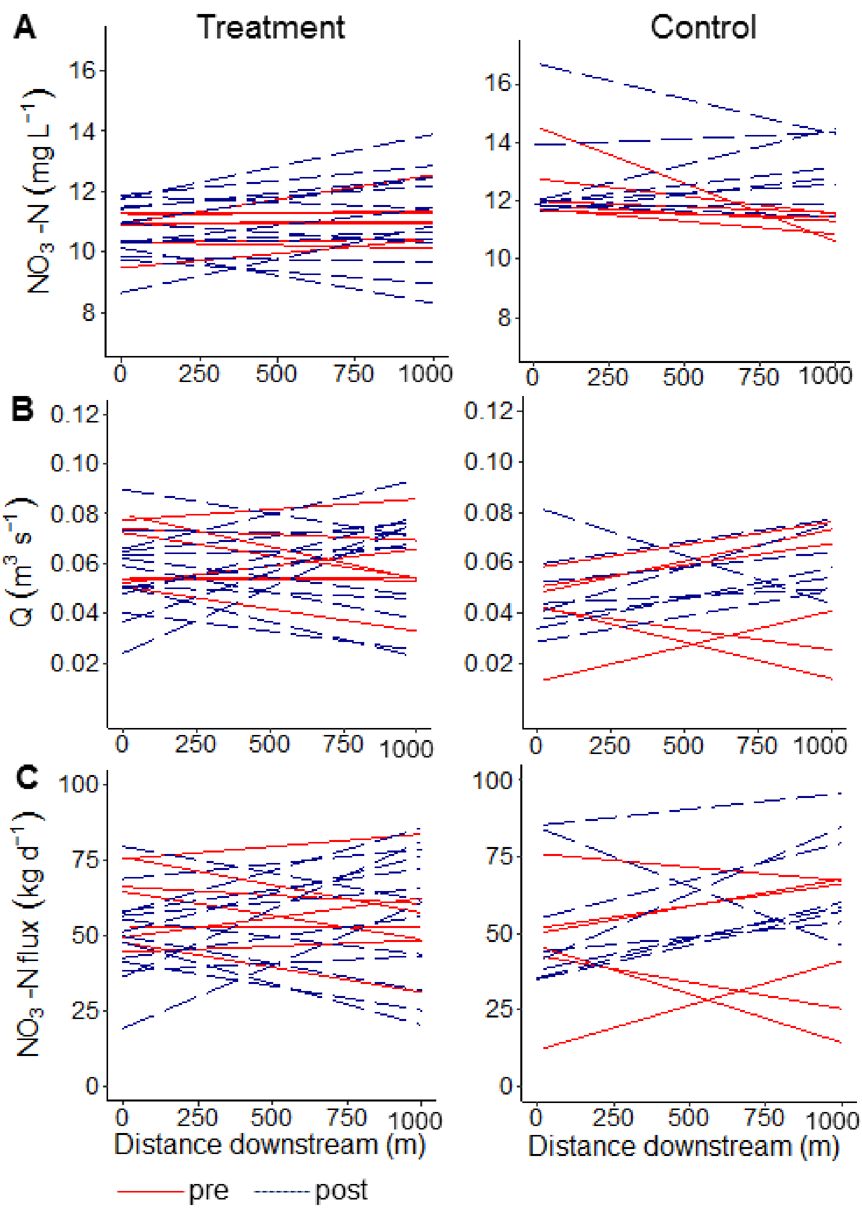

Figure 4.3 Downstream changes in (A) nitrate-nitrogen concentrations, (B) waterway discharge, and (C) nitrate fluxes sampled along two 1000-m study reaches with riparian rehabilitation (treatment) and without (control). Coloured lines correspond to slopes calculated with linear regression using measurements from at least three sampling locations at 0, 500, and 1000 m along sampling reaches on each sampling event. Sampling occurred from January 2014 – October 2015 (pre-rehabilitation; red lines) and October 2015 – October 2017 (post-rehabilitation; blue lines).

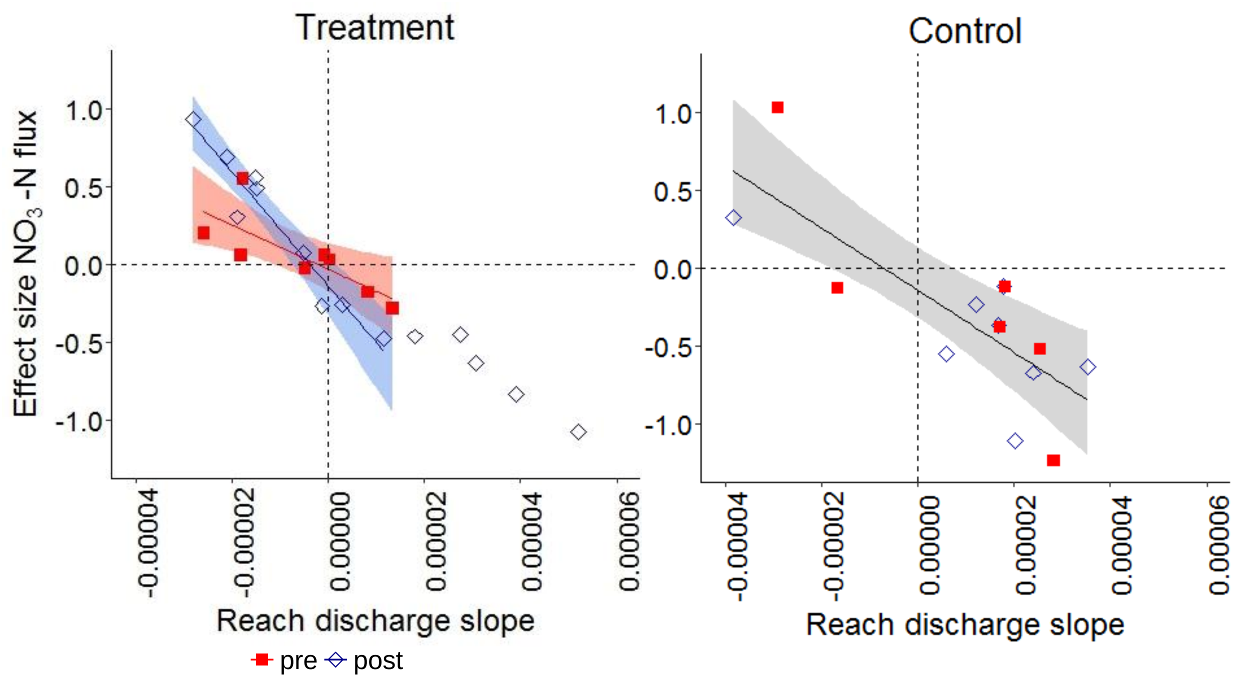

Figure 4.4 Before-after-control-impact comparison of changes in the effect sizes of waterway nitrate-nitrogen fluxes in relation to the slope of change in waterway discharge along two 1000-m study reaches with (treatment) and without rehabilitation (control). Red coloured symbols correspond to reach sampling events pre-rehabilitation from January 2014 – October 2015 compared to post-rehabilitation October 2015 – October 2017 (open symbols). Effect sizes were calculated as: $\log_e$ NO_3-N flux in kg d^{-1} at the upstream end of the 1000-m reach divided by NO_3-N flux (kg d^{-1}) at the downstream end of the 1000-m reach. Effect sizes standardised the net downstream change in waterway N flux for sampling events at different discharges. Dashed horizontal lines across the y-axis indicate no net upstream to downstream change in waterway nitrate flux. The slope of reach discharge was calculated using linear regression of waterway discharge (m^3 s^{-1}) compared to the distance from the top of the 1000-m sampling reaches (m), for sampling locations at 0, 500, and 1000 m downstream, to characterise the net change in reach hydrology for each sampling event. Dashed vertical lines across the x-axis indicate no net upstream to downstream change in waterway discharge. Shaded polygons show significant ANCOVA model fits ($p < 0.05$) with 95 % confidence intervals. Only the shaded regions of reach discharge slopes were analysed in the ANCOVA.

Bioreactor performance: hydrology, nitrate removal, and greenhouse gas fluxes

During the first two years of bioreactor operation from October 2015 – October 2017, water levels within the three bioreactors were weakly related to waterway stage height at the downstream of the 1000-m sampling reach (Y1: n = 12, R^2 = 0.21, p < 0.001; Y2: n = 13, R^2 = 0.44, p < 0.001; Y3: n = 13, R^2 = 0.08, p < 0.001). Bioreactors Y1 and Y3 were inundated more frequently and completely than bioreactor Y2, and HRT for all bioreactors was typically 1 to 6 h (Table 4.2). However, we often observed water ponding above bioreactors Y2 and Y3, indicating that these bioreactors functioned more as wet-spots or sumps in the riparian zone than typical up-flow bioreactors. Therefore, we also suspect that residence times for Y2 and Y3 were likely longer than what we calculated (Table 4.2).

Across all sampling occasions at Y1, mean dissolved oxygen decreased from 5.7 to 1.6 mg L^{-1} across the 12-m length of the bioreactor (n = 12, R^2 = 0.54, p < 0.001; Figure 4.5A). The decrease in nitrate concentration from bioreactor inflow to outflow was weak and variable over time (n = 12, R^2 = 0.07, p = 0.07; Figure 4.5C). There were no changes in DOC (n = 10, R^2 = 0.01, p = 0.55; Figure 4.55B) or SRP (phosphate) concentrations (n=12, R^2 < 0.01, p = 0.97; Figure 4.5D). Over the first two years of operation, we estimate tile drain bioreactor Y1 removed 0.41 kg NO_3-N d^{-1} (95% CI: 0.19 – 0.63), equivalent to ~10 % of the mean daily tile drain nitrate load (Table 4.2). In contrast to the low nitrate removal efficiency, we observed very high nitrate removal rates for bioreactor Y1 ranging from ~22 to ~79 g NO_3-N m^3 d^{-1} (Table 4.2). In comparison, the average nitrate removal efficiencies for the wet-spot bioreactors Y2 and Y3 were 57 % and > 99 %, respectively, assuming the shallow groundwater upwelling into the waterway was the bioreactor water source. For all bioreactors, nitrate removal efficiency (%) increased strongly with HRT (n = 38, R^2 = 0.13, p < 0.05). Nitrate removal efficiency decreased significantly as influent nitrate concentrations increased ($n = 38$, $R^2 = 0.31$, $p < 0.001$), whereas influent water temperature was not related to nitrate removal ($n = 38$, $R^2 < 0.01$, $p = 0.72$). Thus, all bioreactors were effective in mitigating some nitrate from entering the waterway.

The mean greenhouse gas fluxes measured fifteen months post bioreactor installation were 286 mg CO_2-C m^2 h^{-1} and 49 µg N_2O-N m^2 h^{-1} for bioreactor Y1. Comparison of greenhouse gas fluxes from bioreactor Y1 with those from the adjacent farm pasture and native riparian plantings (eight months post-planting) indicated greenhouse gas emissions from the bioreactor were not excessive compared to pasture emissions (H3; Figure 4.6). In contrast, riparian GHG fluxes were significantly lower than pasture and bioreactor Y1 GHG fluxes, with 56 mg CO_2-C m^2 h^{-1} (Kruskal-Wallis $X^2 = 17.82$, df = 2, $p < 0.001$; Dunn's test $p < 0.001$; Figure 4.6A) and 3 µg N_2O-N m^2 h^{-1} (Kruskal-Wallis $X^2 = 14.80$, df = 2, $p < 0.001$; Dunn's test $p < 0.001$; Figure 4.6B). Overall, different rehabilitation tools provided complementary coverage of the key nutrient input pathways along the waterway network and reduced some downstream nitrate export without contributing to GHG pollution swapping.

Table 4.2 Bioreactor performance (means and 95 % confidence intervals) from the first two years of operation from December 2015 – October 2017. Wetted volumes are based on field measurements of bioreactor water levels during the time of sampling. Hydraulic residence time (HRT) estimates for bioreactor Y1 are based on discharge measurements made at the bioreactor outlet; residence time estimates for Y2 and Y3 bioreactors were calculated using Darcy's law for an unconfined system. Nitrate removal estimates for bioreactors Y2 and Y3 are not provided due to uncertainties in residence time. Nitrate, phosphate, and DOC concentrations are from bioreactor outlets.

Bioreactor	**Wetted volume (m^3)**	**HRT (h)**	**NO_3-N ($mg\ L^{-1}$)**	**NO_3-N removal (%)**	**NO_3-N removal rate ($g\ m^{3}\ d^{-1}$)**	**PO_4 ($\mu g\ L^{-1}$)**	**DOC ($mg\ L^{-1}$)**
Y1 tile drain	14.8 (12.9 - 16.8)	0.9 (0.7 - 1.0)	12.5 (12.1 - 12.9)	10.1 (5.9 - 14.2)	50.9 (22.5 - 79.3)	7.2 (2.3 - 12.1)	4.4 (1.5 - 7.2)
Y2 wet spot	6.0 (4.8 - 7.2)	2.7 (2.0 – 3.3)	4.7 (2.3 - 6.8)	57.2 (41.1 – 73.3)	NA	129.7 (<0.1 - 274.9)	6.1 (1.8 - 10.4)
Y3 wet spot	16.3 (13.4 - 19.3)	5.5 (1.7 – 12.6)	0.09 (<0.1 - 0.2)	99.2 (98.2 – 100.2)	NA	615.5 (<0.1 - 1316.4)	67.9 (24.3 - 111.6)

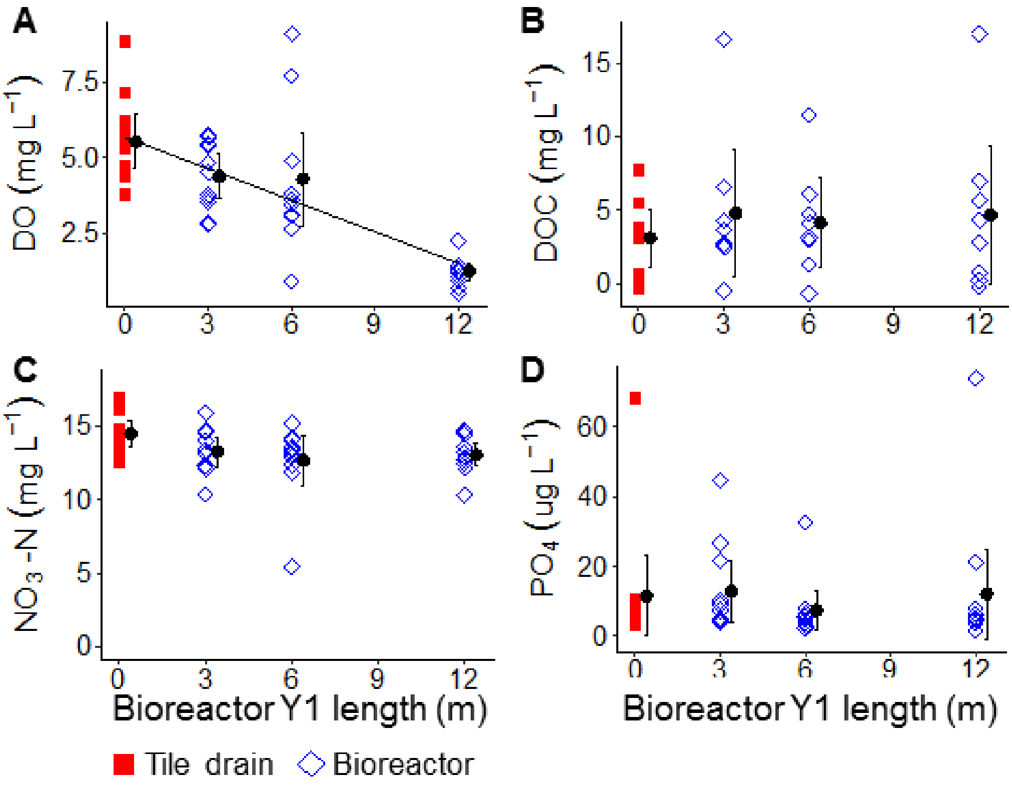

Figure 4.5 Tile drain bioreactor Y1 changes in (A) dissolved oxygen, (B) dissolved organic carbon (DOC), (C) nitrate-nitrogen, and (D) soluble reactive phosphorus (phosphate) from inflow to outflow (distance in minus distance out, m) from December 2015 – October 2017. Red squares are untreated tile drain influent and hollow blue diamonds are samples taken 15 cm from the bottom of the bioreactor along its length. Black dots and bars show mean values and 95 % confidence intervals for each sampling location. Lines indicate the overall model fit from significant linear regression.

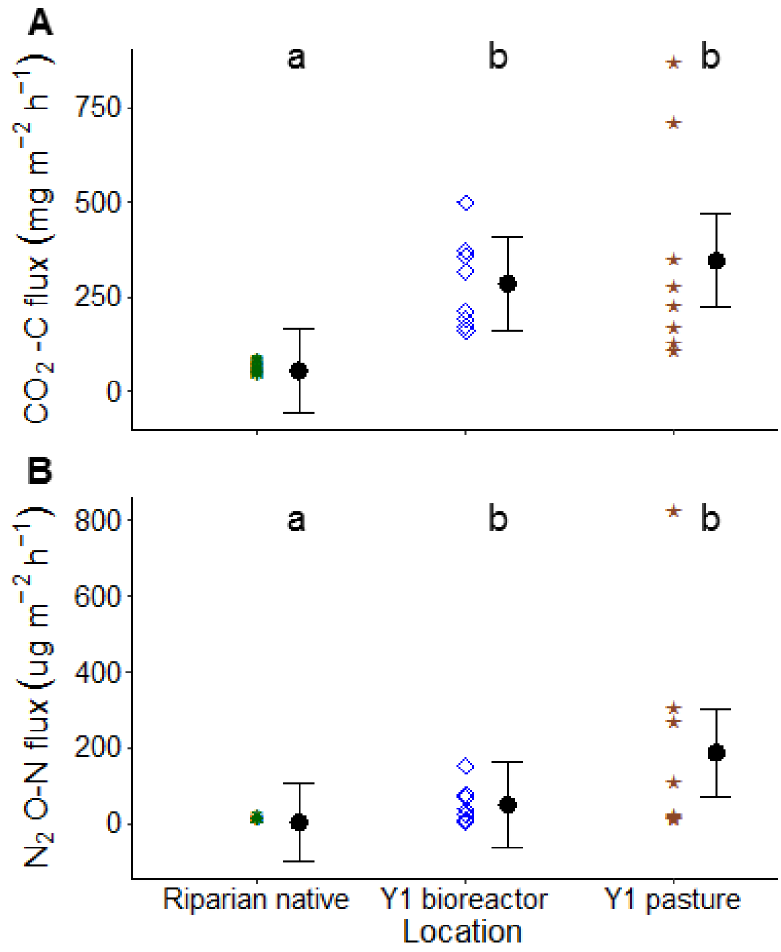

Figure 4.6 Greenhouse gas fluxes of (A) CO_2-C and (B) N_2O-N from soils overlying native riparian plantings, the Y1 tile drain bioreactor, and the surrounding pasture measured 18 January 2017 at the treatment waterway. Coloured symbols represent different sampling locations; black dots and bars show mean values and 95 % confidence intervals; and letters 'a' and 'b' refer to statistically significant different subgroups.

Discussion

Small agricultural waterways and the groundwater, tile drains, riparian seeps, and open tributary drains that they intercept can be significant contributors to high downstream nutrient loads (Blann *et al.*, 2009). However, the available tools and approaches to attenuate nitrate losses from small agricultural headwaters have rarely been implemented in a complementary, multi-scale approach to address these sources along the stream network (Kröger *et al.*, 2015). We used a before-after-control-impact (BACI) approach to test the suitability and performance of three small (< 30 m^3) edge-of-field woodchip bioreactors to complement fencing to exclude livestock from the waterway, streambank re-shaping, and riparian planting practices to attenuate downstream nitrate fluxes from a small agricultural headwater. Overall, hydrological variability, including fluctuations in HRT and changes in stream hydrology, significantly influenced edge-of-field and downstream nitrate attenuation, and nitrate attenuation was only enhanced in the rehabilitated waterway under decreasing reach discharges. The three bioreactors targeting a tile drain and two riparian groundwater upwellings/wet spots had average nitrate removal efficiencies ranging from 10 % to > 50 %. Bioreactor N-removal efficiency was positively correlated with HRT, which varied from 1 – 6 hours among bioreactors. We found that greenhouse gas fluxes of CO_2-C and N_2O-N from a tile drain bioreactor were comparable to emissions from surrounding pastures, whereas riparian GHG fluxes were significantly lower. Overall, our results provide some evidence for the benefits of implementing nitrate attenuation tools at multiple scales along the waterway network at low flows but also highlight the challenges involved. Below, we discuss the key hydrological drivers and limitations of riparian rehabilitation to attenuate high nitrate from groundwater sources, particularly under increasing stream flows.

In small agricultural waterways, nitrate removal in riparian zones can remove more nitrate than in-stream processes, but, these removal rates decline with high stream flows (Ranalli & Macalady, 2010). Therefore, besides intercepting nutrients along different flow paths at key places along the stream network, implementing different types of tools may be necessary to achieve nutrient removal under different hydrological conditions (Craig *et al.*, 2008). The combination of stream rehabilitation tools we implemented enhanced reach nitrate flux attenuation (H1) under losing water conditions post-rehabilitation compared to pre-rehabilitation, whereas there were no significant changes in nitrate flux in the control waterway. However, the effectiveness of these tools to attenuate nitrate fluxes diminished with greater gaining reach discharge and shorter HRT in the bioreactors. At higher flows, bioreactors and riparian planting likely only intercepted a small portion of the groundwater inputs and N flux to the treatment waterway. In both waterways, high groundwater nitrate inputs and increases in net discharge through the reach meant that waterways became net exporters of nitrate during times of high flow. This strong influence of regional groundwater on waterway nitrate flux dynamics highlights the need for better land-based nutrient management, especially in catchments with poor conditions for denitrification or N-attenuation in groundwater (Di & Cameron, 2002; Rivett *et al.*, 2008). However, high groundwater nitrate fluxes will likely continue to be problematic to due time lags and the 'load to come' (Schiel & Howard-Williams, 2016). Therefore, the substantial nitrate fluxes from upstream springs (groundwater), as well as from tile and open tributary drains, should be targeted for management at the farm-scale to complement catchment-scale and land-based nitrate mitigation measures. Our results emphasize the importance of contextualising and targeting local hydrology and nutrient flux patterns when implementing and evaluating riparian rehabilitation tools to attenuate nutrient export. Furthermore, our results indicate that there is potential to develop better or more effective nitrate-removal tools that can be scaled-up along and within the waterway network, and there are also substantial challenges in doing this under very high nitrate loads.

A ubiquitous obstacle to stream nutrient attenuation approaches is targeting stream rehabilitation that can accommodate the inherent ecosystem variability, such as seasonal and longitudinal changes in hydrology, at the influential scales and locations along the waterway network (Filoso & Palmer, 2011; Doyle & Shields, 2012). We accounted for intra- and inter-annual differences in nitrate-N loads due to seasonal changes in the baseflow of these spring-fed waterways (Chapter Three), since both waterways were sampled before and after the rehabilitation was implemented. Since N-loads in these waterways are also impacted spatially by the inputs of N from springs, seeps, and groundwater inputs (Chapter Three), we examined how changes in the prevailing waterway hydrology (ANCOVA covariate) influenced the change in N-flux from the top to bottom of our 1-km study reaches (ANCOVA response). However, due to potential between-catchment differences in spring N-inputs along reaches, a key assumption of our BACI approach was that the treatment and control waterways were impacted similarly by these intra- and inter-annual groundwater dynamics. We propose that this assumption was met, since waterways were located 10-km apart and were impacted by similar changes in seasonal baseflows and groundwater N inputs during the study (Chapter Three). Overall, accounting for catchment-scale drivers and their spatiotemporal variability is critical to detect the success of stream rehabilitation to restore processes like nutrient retention and removal (Bernhardt & Palmer, 2011).

Although rehabilitating headwater reaches may be an effectual approach to attenuate downstream nutrients (Thomas, 2014; O'Brien *et al.*, 2017), we found limited success of riparian rehabilitation tools in our treatment waterway. In the treatment waterway, nitrate attenuation was enhanced for a given set of hydrological conditions on only five of the fourteen sampling occasions post-rehabilitation, and these five occasions were all characterised by 'losing' water conditions along the reach (Figure 4). Most likely, attenuation was only boosted under these low-flow settings because of the enhanced surface-area-to-volume ratio, increased contact with the benthos, and longer HRT under these conditions relative to higher flows (Royer *et al.*, 2004). Moreover, riparian rehabilitation is also more effective at removing nitrate via denitrification at decreasing stream flows (Ranalli & Macalady, 2010). Given the prominent influence of stream hydrology on nutrient attenuation across riparian networks, as well as the consistently-high nitrate loads from springs and regional groundwater generally, other combinations of rehabilitation tools might improve in-stream nitrate attenuation. This may involve combinations of tools that can intercept and store surface runoff or subsurface drainage, and increase HRT in the riparian zone, as well as providing a carbon source, water retention, and increasing contact with denitrifying microbes in-stream (Kröger *et al.*, 2015; Faust *et al.*, 2017). However, given the larger-scale drivers of catchment hydrology and contributions from regional groundwater to nitrate export, we propose that managers will need to recognise and accept that multiple-tool, multiple-scale stream rehabilitation in agricultural headwaters will have limitations to attenuating nitrate export.

Experimental trials of bioreactors with riparian management actions that reflect on-the-ground realities and management contexts are rare, yet urgently needed (David *et al.*, 2015). In flat agricultural landscapes with limited space for natural water retention along or within the waterway, bioreactors are particularly well-suited to complement riparian rehabilitation (Goeller *et al.*, 2016). Here, we implemented one small tile drain bioreactor and two wet-spot bioreactors to target nitrate RTPs that were bypassing the riparian protection network. The bioreactors were implemented at relatively low cost and within a realistic management context (i.e., as part of a working farm), rather than as fully-instrumented experimental bioreactors commonly reported on in the literature (Higgins *et al.*, 2017). Although we acknowledged and accepted uncertainties about bioreactor source water chemistry in our design, we confirmed (H2) that the tile drain bioreactor removed nitrate from edge-of-field sources that would have otherwise been added to the receiving waterway. Although the 10 % mean nitrate removal efficiency for this bioreactor was lower than the average 33 % removal efficiency from other field-scale tile drain bioreactors (Woli *et al.*, 2010; Christianson *et al.*, 2012b; David *et al.*, 2015), surprisingly, the mean nitrate removal rate of 50 g N m^{-3} d^{-1} was much higher than the 4.7 g N m^{-3} d^{-1} reported in a meta-analysis of bioreactor performance (Addy *et al.*, 2016). Hence, many small bioreactors implemented at low cost (i.e., $100s to $1000s per bioreactor; Appendix 1) may offer better performance than a few, expensive, large bioreactors at the catchment-scale. Thus, the trade-off between bioreactor size and performance will be important to consider for future installation.

We observed significant variation in nitrate removal performance ranging from < 1 up to more than 79 g N m^{-3} d^{-1}, which was consistent with other field-scale bioreactors, where variations in temperature and inflow water chemistry resulted in removal rates ranging from 0 – 72 g N m^{-3} d^{-1} (Hassanpour *et al.*, 2017). The variable bioreactor performance we observed was likely due to short hydraulic residence times, rather than cold temperatures or low influent nitrate. Hence, optimising HRT by increasing bioreactor length or the amount of wetted bioreactor volume could be practical solutions to retrofit or adaptively manage these bioreactors (Christianson *et al.*, 2012a). Moreover, one of the reasons why nitrate attenuation was limited at high flows was because of low HRT. However, while nitrate management decisions require confidence around bioreactor performance, we propose that implementing bioreactors and accepting some uncertainties around their performance likely provides greater net environmental benefits than not implementing bioreactors in the first place. Furthermore, elucidating the in-stream impacts and other environmental performance trade-offs of field-scale bioreactors are more worthwhile to inform stream rehabilitation programmes than detailed investigations of their internal hydrology and nutrient removal, which are already relatively well-known (Addy *et al.*, 2016). Therefore, we also examined the potential pollution swapping potential of bioreactors implemented in the context of riparian rehabilitation.

Understanding the pollution swapping potential of nutrient attenuation tools as compared to agricultural sources is important to evaluate their overall environmental impacts (Fenton *et al.*, 2016). Gaseous emissions of CO_2 and N_2O from bioreactors can be significant, given that these often have high DOC and operate under a range of redox conditions associated with variable discharge and influent water chemistry (Moorman *et al.*, 2010; Warneke *et al.*, 2011b). Nevertheless, we confirmed (H3) that bioreactor GHG fluxes of CO_2-C and N_2O-N were not higher than existing agricultural sources along the waterway. The GHG fluxes from soils above bioreactors and pastures were within the ranges reported from other bioreactors, agricultural land, constructed wetlands, and nitrate-polluted streams (Elgood *et al.*, 2010; Groh, Gentry & David, 2015), whereas GHG fluxes from riparian plantings with native vegetation were significantly lower. Although we were limited to one sampling occasion, the riparian GHG fluxes we measured (56 mg C m^2 h^{-1}) were comparable to mean CO_2-C fluxes (83 mg C m^2 h^{-1}) measured from native riparian plantings from a Canterbury-wide survey (Burrows, 2017). The same was true for riparian fluxes of N_2O-N (this study: 3 μg N m^2 h^{-1}; Canterbury survey: 15 μg N m^2 h^{-1}) (Burrows, 2017). The differences in greenhouse gas production we measured highlight the importance of understanding the environmental impacts and pollution-swapping trade-offs of nitrate loss mitigation tools.

Besides GHG, bioreactors can also be sources of high chemical or biological oxygen demand, low pH, phosphorus, or undesirable redox products like hydrogen sulphide and methyl mercury (Robertson & Merkley, 2009; Healy *et al.*, 2012). These environmental stressors that might be released from bioreactors may have deleterious effects on the ecological health of waterways (Goeller *et al.*, 2016), but, we did not measure problematic changes in waterway dissolved oxygen, pH, or phosphate levels at our treatment waterway. As the implementation of multiple bioreactors in series along agricultural waterways increases, future ecological assessments should aim to detect significant impacts of bioreactor performance on key indicators of stream ecosystem health, including nutrient processing, organic matter breakdown, stream metabolism, and invertebrate and fish assemblage structure and function (Chapter Two). Overall, the likelihood of bioreactors and riparian planting combining to generate desirable improvements in multiple ecosystem functions such as enhanced nutrient cycling to improve water quality and ecosystem health may ultimately depend on implementing different tools in a complementary approach, where combinations of tools target the nutrient delivery pathways at their influential scales along and within agricultural waterways and in ways that are designed to accommodate local hydrological conditions.

In conclusion, stream hydrology is a key driver of nutrient export in small, agricultural waterways, with lower-flows and longer HRT associated with greater nutrient retention and removal for both in-stream and edge-of-field sources, respectively (Royer *et al.*, 2004; Woli *et al.*, 2010). In addition to matching rehabilitation tools to suit the prevailing stream hydrology, managers need information to contextualise how implementing multiple, different, riparian rehabilitation tools can enhance nutrient attenuation along the stream network, which should also improve in-stream nutrient attenuation (Lammers & Bledsoe, 2017). We found evidence that a multiple-tool, multiple-scale stream rehabilitation approach with bioreactors implemented together with riparian rehabilitation influenced greater nitrate flux depletions in a nitrate-polluted, agricultural headwater post-, compared to pre-rehabilitation, but only under low flow conditions. In comparison, there were no significant changes in nitrate flux in the control waterway under any flow condition. In both the control and treatment waterways at all times, N fluxes increased when reaches gained water downstream. Although we could not disentangle the individual contributions of bioreactors as compared to riparian plantings, our research delivered the first insights into how the implementation of complementary nitrate attenuation tools (specifically bioreactors and riparian planting) may together influence downstream water quality, even in a context/region with high groundwater nitrate inputs. However, due to the ineffectiveness of riparian rehabilitation or in-stream processes to attenuate nutrients under increasing stream flows and shorter HRT (Royer *et al.*, 2004; Ranalli & Macalady, 2010), as well as the practical bioreactor implementation necessities of simplicity, cost efficiency, and low maintenance, we emphasize that managers need to recognize the limitations of stream rehabilitation to attenuate catchment nutrient loads. Future research should investigate how combinations of rehabilitation tools can be matched or 'stacked' to increase water retention, promote contact with the benthos, and enhance organic matter or carbon stocks to improve nitrate attenuation across riparian networks (Kröger *et al.*, 2015; Faust *et al.*, 2017). Overall, our results show the potential of implementing multiple nutrient mitigation tools to accrue desired environmental benefits, such as improving in-stream water quality and reducing GHG. Such a toolbox approach to waterway nutrient management is transferable to other small agricultural waterways where stream rehabilitation programmes must fit within working agricultural landscapes with limited space for natural water retention options or narrow riparian buffers.

Supplement to Chapter Four

Table S4.1 Bioreactor construction specifications and design limitations. Costs are for bioreactor construction only.

Bioreactor	Treatment area (ha)	Treatment source/location	Bioreactor dimensions (m)	Woodchip volume (m^3)	Inlet & outlet manifold	Cost (NZD)	Design limitations
Y1	6	tile drain	10 x 2.5 x 1	25	2 m of 15-cm diameter perforated drain pipe along bottom	$2600	Mixing of untreated tile drain water with treated bioreactor effluent along the 10 m flow path from bioreactor outlet to receiving waterway
Y2	NA	riparian groundwater upwelling/seep	10 x 2 x 1	20	None	$1200	Intercepting the predominant flow path of shallow groundwater from the riparian zone to the stream; proportional exchange of untreated and treated flows along the lengths of each bioreactor
Y3	NA	riparian groundwater upwelling/seep	12 x 2 x 1	22	None	$1300	Intercepting the predominant flow path of shallow groundwater from the riparian zone to the stream; proportional exchange of untreated and treated flows along the lengths of each bioreactor

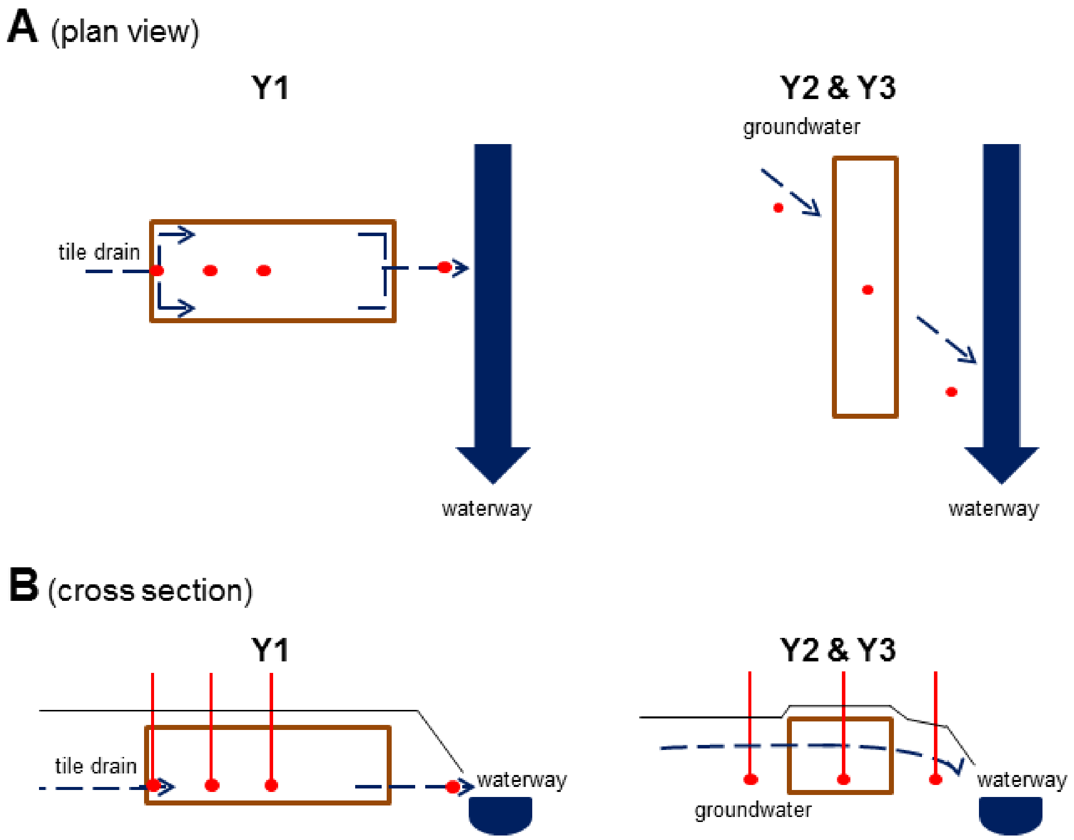

Figure S4.2 Bioreactor sampling location in piezometers, indicated by red dots, for Y1, Y2, and Y3, shown in plan view (A) and cross section (B). Subsurface flowpaths (e.g., tile drain, groundwater) are indicated with blue dashed lines, and surface flow paths (e.g., waterway) are indicated by solid blue lines.

Plate 5. In-stream wood added along 100-m reaches in four agricultural waterways in spring 2016. Different panels show different waterways.

Photo: Brandon C. Goeller

Chapter Five:

Adding in-stream wood enhances removal of nitrate, but only sporadically, in spring-fed, agricultural headwaters

Introduction

Excess reactive nitrogen (N) and phosphorus (P) from agricultural land-use has degraded water quality and caused problematic eutrophication around the world (Rockström *et al.*, 2009; Glibert, 2017). In agricultural landscapes, drainage ditches and small streams are important catchment headwaters that can disproportionately influence downstream nutrients and ecosystem processes that affect nutrient cycling (Dodds & Oakes, 2008; Woodward *et al.*, 2012). To mitigate nutrient losses to these waterways, land-based pollution source controls attempt to limit nutrient inputs (e.g., fertilizer reductions) (Conley *et al.*, 2009). However, attenuating downstream nutrient loads with farm-based nutrient source controls is often challenging. For example, time lags in groundwater nutrient inputs to waterways and degraded riparian and in-stream ecological conditions can limit nutrient removal and retention along and within the stream corridor (Bernot & Dodds, 2005; Withers *et al.*, 2014). Overall, agricultural waterways very often have impaired capacity to remove nutrients through nutrient cycling or biological 'self-cleansing' (Bernot *et al.*, 2006; von Schiller *et al.*, 2017). Thus, there is an opportunity for stream rehabilitation tools that enhance ecosystem processes controlling nutrient cycling to attenuate downstream nutrient loads and eutrophication (Filoso & Palmer, 2011; Lammers & Bledsoe, 2017). However, stream rehabilitation actions have often had uncertain or unclear outcomes, since excess nutrients can impair several ecosystem functions and rehabilitated waterways may not respond in a predictable way (Palmer & Febria, 2012).

One approach to boost nutrient cycling could be to add organic carbon (OC) and thereby enhance the conditions for biota to sequester nutrients within the stream network (Craig *et al.*, 2008; Lammers & Bledsoe, 2017; O'Brien *et al.*, 2017). To sustain the larger-scale (e.g., downstream or catchment) and longer-term benefits of nutrient rehabilitation, interventions should aim to enhance activated zones or ecosystem 'control points' of nutrient removal. This approach could create a gradient of biogeochemical activity that responds to critical drivers of nutrient cycling along or within the stream network and over time (Bernhardt *et al.*, 2017). Organic carbon availability boosts stream microbial nutrient processing and plays a central role in governing nutrient cycling and stream metabolism (Johnson *et al.*, 2012; Stanley *et al.*, 2012; Mineau *et al.*, 2016). However, our ability to assess and manage how stream nutrient cycling and related ecosystem functions might respond to rehabilitation tools such as organic matter (OM) additions or organic carbon (OC) amendments is limited (Stanley *et al.*, 2012). This is despite the increasing prevalence of organic matter amendments in stream nutrient mitigation and rehabilitation (Lammers & Bledsoe, 2017; Faust *et al.*, 2017).

In many streams, a substantial fraction of the dissolved organic carbon (DOC) originates from terrestrial (allochthonous) OM (Aitkenhead-Peterson, McDowell & Neff, 2003; Bernal *et al.*, 2018). In forested catchments, small wood such as sticks and twigs can make up a large fraction of the allochthonous OM inputs, dominating the standing stock of benthic OC and contributing substantially to stream DOC fluxes (Bilby, 2003; Elosegi, Díez & Pozo, 2007). Stream wood can be an important source of DOC, and can stimulate nutrient cycling and enhance nitrate removal through multiple pathways (Elosegi *et al.*, 2007). Wood provides surface area for epixylon biofilms (Eggert & Wallace, 2007), serving as an important substrate for microbial metabolic activity (Tank *et al.*, 2010). However, the clearance of riparian forests and the drainage of wetlands disconnects agricultural waterways from key terrestrial carbon (C) sources in floodplains and riparian corridors (Stutter *et al.*, 2018).

Furthermore, the channelization and mechanical clearance of agricultural waterways often remove in-stream structures and pools that might trap and retain organic matter (Blann *et al.*, 2009). Hence, wood and wood-derived OM are typically absent from agricultural waterways, where channel clearance and drain maintenance prevail over establishing natural in-channel features to retain and cycle OM and nutrients (Ensign & Doyle, 2005; Kröger *et al.*, 2011). Thus, C is less available for N and P cycling, and this imbalance in macronutrients can limit stream heterotrophic processing (Stutter *et al.*, 2018).

Inputs of OM might overcome C-limitation and influence stream nutrient cycling in nutrient-rich agricultural waterways (Faust *et al.*, 2016; O'Brien *et al.*, 2017). In a global meta-analysis of macronutrient stoichiometry, Stutter and others (2018) concluded that nutrient cycling becomes impaired when OC stocks are depleted or nutrient inputs of N and P exceed biological demands (e.g., nutrient saturation) (Earl *et al.*, 2006). Therefore, C additions in these waterways should provide process-based rehabilitation which stimulates nutrient retention and removal (Fork & Heffernan, 2014; Waters *et al.*, 2014; O'Brien *et al.*, 2017). Rehabilitation of agricultural drainage ditches could boost their performance as 'linear wetlands', with enhanced microbially-mediated nutrient cycling potentially occurring in sediments in the streambed, banks, riparian soils, and floodplains (Roley *et al.*, 2012; Kröger *et al.*, 2015; Schilling *et al.*, 2018). However, evidence is needed to show how adding OM could attenuate in-stream nutrients, especially given the strong hydrologic controls on nutrient fluxes and water retention time at larger (e.g., reach, catchment) scales (Chapter Three, Chapter Four).

Nutrient removal and retention in small waterways can be very dynamic, however, driven by fluctuations in the prevailing stream hydrology (Mulholland & Hill, 1997; Royer *et al.*, 2006). Furthermore, changes in the availability of OC and nutrients in particular locations and times likely influences the extent to which ecosystem 'control points' of nutrient cycling are activated (Newcomer Johnson *et al.*, 2016; Bernhardt *et al.*, 2017). The enhancement of nutrient cycling via substrate and DOC from wood might fluctuate in the spatial extent of where nutrient removal occurs and times when conditions are conducive to nutrient cycling (Bernhardt *et al.*, 2017). Thus, identifying times and places where OM can enhance N cycling in agricultural streams will be important.

Macronutrient imbalances are common in small agricultural waterways, which often have high N and P, low DOC, and poor water retention times required for nutrient cycling (Kröger *et al.*, 2007; Warrner *et al.*, 2009; Faust *et al.*, 2018). Hence, these waterways have limited nutrient retention or removal efficiency, or nutrient uptake may be saturated (Bernot *et al.*, 2006). Despite the importance of DOC and the widespread consequences of OC limitation in agricultural waterways, relevant information to manage these ecosystems are surprisingly sparse (Stanley *et al.*, 2012; Faust *et al.*, 2018). Managers need information around how, when, and where nutrient cycling is enhanced in rehabilitated streams to inform adaptive management (Stanley *et al.*, 2012; Lammers & Bledsoe, 2017). We are unaware of other studies that have added wood to agricultural waterways with the explicit goal of promoting nutrient retention and removal or which have evaluated rehabilitation outcomes with an ecosystem approach shedding light on the locations and times where stream rehabilitation can attenuate downstream nutrients.

We experimentally added OM as small wood (woodchips) to stimulate ecosystem processes to enhance nutrient removal and retention in small, agricultural, spring-fed, headwater waterways as part of the Canterbury Waterway Rehabilitation Experiment (CAREX). Ecosystem processes linked to nutrient removal and retention are inherently variable, and they are influenced by some combination of C, N, and P availability, biophysical processes, as well as microbially-mediated and invertebrate-driven processes. Therefore, we evaluated the temporal and spatial variability in responses to added in-stream wood to stimulate N, P, and DOC cycling at the reach-scale. We hypothesized that in-stream wood addition would stimulate activated zones or control points in agricultural waterways characterized by boosted nitrate removal at different times and with different spatial extents in reaches across waterways. By increasing the standing stocks of terrestrial OM and helping overcome C-limitation, we anticipated that phosphate and DOC would also be removed or retained in treatment reaches downstream of the wood, and that phosphate and DOC removal or retention patterns would change along reaches, and over time.

Methods

Study design

Our study was conducted on the Canterbury Plains, on the east coast of the South Island, New Zealand. Originally formed from Quaternary gravel outwash deposits, the Canterbury Plains are the largest area of flat land in New Zealand. The Plains were covered by wetlands and native forest, but since European settlement in the 1850's, the land has been used primarily for pastoral agriculture (Pawson & Holland, 2008). The region has recently grown into an important centre for dairy farming (Livestock Improvement Corporation & Dairy NZ, 2016). Canterbury has a cool and dry climate with a mean annual temperature <12°C and receives annual rainfall of 681 – 895 mm (Macara, 2016). Although very productive, the light, stony soils of the Canterbury Plains have limited water holding capacity (Webb, 2008). Hence, nitrate leaching from intensified farming is a major problem for groundwater and surface water quality (Carrick *et al.*, 2013; Scarsbrook *et al.*, 2016). Canterbury's agricultural practices have become highly intensified with limited natural water retention and treatment options in the riparian zone or within waterways, due to land clearance and drainage (Pierce *et al.*, 2012). Networks of agricultural drains, ditches, and subsurface tile drains form the headwaters of many catchments in lowland Canterbury (Winterbourn, 2008). These waterways have been negatively impacted by nuisance aquatic weeds, deposited fine sediments, high nitrate-nitrogen levels above the human drinking water guideline of 11.3 mg L^{-1} NO_3-N (World Health Organization, 2017), and have depauperate freshwater communities (Burdon *et al.*, 2013). Thus, balancing agricultural production with water quality and freshwater ecosystem service provision poses substantial management challenges in this region (Ausseil *et al.*, 2013).

Our experiment was set up as a nested design, where paired control and treatment reaches were nested within four replicate waterways, and impacts on water column nutrients were assessed monthly for six months. In austral spring 2016, we experimentally added untreated *Pinus radiata* woodchips to boost in-stream organic matter in four small, agricultural waterways characterized by high nitrate and low DOC (Table 5.1). The study waterways had been previously fenced to exclude livestock, had vegetated riparian buffers 2 – 4 m wide containing grasses, gorse (*Ulex europaeus*), sedges (*Carex* spp.), flax (*Phormium* spp.), and toetoe (*Austroderia* spp.), and were part of ongoing waterway rehabilitation efforts as part of CAREX. Because these waterways were managed primarily as agricultural drains, they were channelised and lacked in-stream structures, pools, and terrestrial organic matter. Furthermore, the waterways were mechanically cleared on an annual basis to remove excessive weedy aquatic macrophytes, thereby removing entrained terrestrial OM as well. However, macrophytes were not cleared in the study portions of the waterways during the experiment.

Table 5.1 Waterway hydrological, physical, and nutrient characteristics summarised for the eight 400-m reaches before wood was experimentally added in spring 2016. Data are summarised by waterway (two-letter codes) for paired treatment (T) and control (C) reaches.

Characteristic	**BO (T)**	**GR (T)**	**PY (T)**	**YM (T)**	**BO (C)**	**GR (C)**	**PY (C)**	**YM (C)**	**Treatment mean**	**Control mean**
Wetted width (m)	1.5	1.6	1.6	1.7	1.4	1.7	1.0	1.6	1.6	1.4
Depth (m)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Velocity (m s^{-1})	0.2	0.3	0.3	0.3	0.1	0.3	0.1	0.4	0.3	0.2
Discharge (L s^{-1})	15.0	66.0	35.0	68.0	5.4	65.0	15.0	65.0	46.0	37.6
Median particle size, D_{50} (mm)	5.6	26.5	2.0	28.5	13.0	65.0	10.8	53.9	15.7	35.7
Fine (< 2mm) sediment cover (%)	22.0	41.0	7.0	4.0	76.0	58.0	57.0	11.0	18.5	50.5
Leafpacks (%)	1.0	<1.0	<1.0	<1.0	<1.0	<1.0	4.0	<1.0	0.3	1.0
Small wood (%)	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Algae and moss (%)	19.0	9.0	37.0	16.0	17.0	30.0	5.0	5.0	20.3	14.3
Canopy cover (%)	59.2	<1.0	35.2	<1.0	<1.0	<1.0	<1.0	<1.0	23.6	0.0
Bank macrophyte cover (%)	8.0	<1.0	<1.0	<1.0	<1.0	<1.0	34.0	<1.0	2.0	8.5
Bed macrophyte cover (%)	<1.0	9.0	7.0	6.0	40.0	7.0	38.0	3.0	5.5	22.0
NO_3-N (mg L^{-1})	16.2	12.6	11.7	10.9	16.4	13.4	11.8	10.7	12.9	13.1
PO_4 (µg L^{-1})	3.2	3.0	1.1	3.9	0.1	2.6	1.1	2.8	2.8	1.7
Dissolved organic carbon (mg L^{-1})	2.4	2.0	2.5	2.2	1.9	1.1	2.3	1.9	2.3	1.8

Pre-rehabilitation assessment of reach hydrology, physical, and nutrient characteristics

Each waterway was assigned a 400-m upstream reach (control, no wood addition) and a 400-m downstream experimental reach (treatment, wood addition). We selected study reaches to ensure that waterway characteristics (e.g., riparian vegetation, in-stream substrate, mean wetted width) were comparable between reaches and waterways. Also, reaches were located where no open tributary drains and few or no subsurface tile drains entered the reach. However, all waterways were spring-fed and received consistently high inputs of nitrate from regional groundwater (Chapter Three).

We sampled a representative 20-m reach within each of the 400-m study reaches to characterise overall hydro-physical and nutrient characteristics one month before the experiment started in the austral spring of 2016. Within each 20-m reach, we measured the stream wetted width and depth in a single transect across the thalweg, with water velocity assessed across this transect using a Flow-Mate 2000 (Marsh-McBirney, USA). Waterway discharge (m^3 s^{-1}) was calculated according to the area integration method (Gordon *et al.*, 2012). A 'Wolman walk' was conducted to estimate the median substrate particle size by collecting 50 particles from the streambed randomly along the 20-m reach (Wolman, 1954). We selected five, 30 x 30 cm quadrats (total area 0.45 cm^2) in each reach in a stratified-random fashion (Niyogi *et al.*, 2007) to conduct visual assessments of fine (< 2 mm) sediment cover, CPOM (e.g., leafpacks, small wood), algae, moss, and bed and bank macrophytes. We measured channel shading in the centre of the channel using a densitometer (Lemmon, 1956).

Nutrient concentrations of nitrate-nitrogen, soluble reactive phosphorus (SRP as phosphate), and DOC were measured from one grab sample taken within the 20-m reach. Water samples for nitrate-nitrogen and phosphate analysis were filtered through Whatman glass fibre fine

(0.7 μm) filters in the field, transported on ice, and frozen in acid-washed (5% HCl) plastic bottles until analysis. Nitrate-nitrogen and soluble reactive phosphorus (SRP, phosphate) were analysed colorimetrically on an Easychem Plus analyser (Systea, Italy) at detection limits of 0.01 mg L^{-1} NO_3-N and 0.1 μg L^{-1} PO_4, respectively. Dissolved organic carbon samples were filtered with Whatman glass fibre fine (0.7 μm) filters into acid-washed (5% HCl) amber glass vials and transported on ice. Dissolved organic carbon samples were acidified to a pH of 2-3 with 100% HCl in the laboratory and stored at 4 °C until analysis within 2-3 months (US EPA, 2003). Dissolved organic carbon was measured by catalytic oxidation with the TC-IC method (Shimadzu, Japan) at a detection limit of 4 μg L^{-1}. Samples analysed for DOC in March and April were analysed at Lincoln University using a Vario TOC cube (Elementar, Germany) with the TC method at a detection limit of 6 μg L^{-1}.

Waterways were small (1.0 – 1.7 m wide), shallow (< 0.3 m deep), and slowly to moderately-slowly flowing (5.4 – 68.0 L s^{-1}), and the hydrology and substrate were comparable in paired reaches within waterways (Table 5.1). The streambed in experimental and control reaches were generally stony-bottomed (D_{50} 2.0 – 65.0 mm), although some fine sediment cover was present (particles < 2 mm: 4.0 – 76.0 %) (Table 5.1). The coverage of weed macrophytes, predominantly introduced emergent species monkey musk (*Erythrante guttata)* and watercress (*Nasturtium microphyllum*), growing on the streambed and streambanks was < 40 % aerial coverage (Table 5.1). At the start of the experiment, nitrate-nitrogen concentrations were high in all study reaches (NO_3-N: 10.7 – 16.4 mg L^{-1}; Table 5.1). In contrast, SRP and DOC were very low, ranging from 0.1 – 3.9 μg L^{-1} phosphate and 1.1 – 2.5 mg L^{-1} DOC across reaches (Table 5.1). Before the wood addition, the standing stocks of coarse particulate organic matter (CPOM) were <1 % aerial coverage in experimental and control reaches (Table 5.1), and the standing stocks of allochthonous OM and DOC were very low overall.

Assessing wood breakdown and changes in reach macronutrients

We artificially boosted in-stream organic matter to test whether overcoming carbon limitation would enhance in-stream nitrate removal. Provided that this is possible, we intended to use this information to inform simple and pragmatic stream rehabilitation tools in waterways with high nitrate loadings from catchment and groundwater or spring sources (Chapter Four). Woodchips were added throughout the upper 100 m of our 400-m treatment reaches in the austral spring of 2016. Spun polyester onion bags (43 x 25 cm) were packed with 1400 – 1500 g dried woodchips, and ~130 bags were added over the upper 100 m of each 400-m treatment reach. The bags were secured to the streambed with 12 mm rebar pegs spaced every 2 m downstream on alternating sides to encourage a meandering stream flow. This amount of wood (~1.5 m^3 woodchips or ~180 kg dry mass) was equivalent to a wood loading of approximately 100 m^3 wood ha^{-1} of the wetted stream channel, an in-channel wood volume typical for mature pine forests and native forests in South Island, New Zealand (Evans, Townsend & Crowl, 1993). In New Zealand, *Pinus radiata* is a common commercial forestry plantation species, and it is functionally equivalent to native tree species in terms of wood biofilm and stream invertebrate colonisation (Collier, Smith & Halliday, 2004).

Each treatment reach contained a subset of eighteen bags that were pre-dried and weighed to 1500 g. Three of these pre-weighed bags were randomly removed from each treatment reach at one, three, and six months post-implementation to assess wood breakdown rates across waterways. At the time of collection, the bags were gently rinsed in the waterway to remove accumulated fine sediment, algae, and invertebrates. Woodchips were stored in a glasshouse at 25 °C for three to five days before being dried at 50 °C for four days in a drying oven. The total dry weight of woodchips from each bag was recorded to nearest 1.0 g, and used to calculate woodchip breakdown rates for each waterway following Petersen and Cummins (1974).

Waterway sampling aimed to detect reach-level changes in water column macronutrients associated with the wood addition. We sampled multiple locations, at increasing distances downstream along each reach, monthly for six months to detect both spatial and temporal changes in nutrient cycling in the paired control and treatment reaches within the four waterways. Samples were taken at 0, 100, 150, 250, and 400 m downstream within each reach (Figure 5.1). At each sampling location, we measured temperature, dissolved oxygen, electrical conductivity, pH, and turbidity with multi-probes (YSI, Yellow Springs, USA). Turbidity was measured from grab samples with a portable infrared light meter (Eutech, Singapore) at a detection limit of 0.01 NTU. We took grab samples to evaluate nutrient concentrations of nitrate-nitrogen, SRP, and DOC. Following water quality and nutrient sampling, we measured the wetted width, depth, and flow velocity at each sampling location, and calculated discharge (m^3 s^{-1}) according to the area integration method (Gordon *et al.*, 2012). Nitrate fluxes were calculated by multiplying nutrient concentrations by the discharge measured at each sampling location.

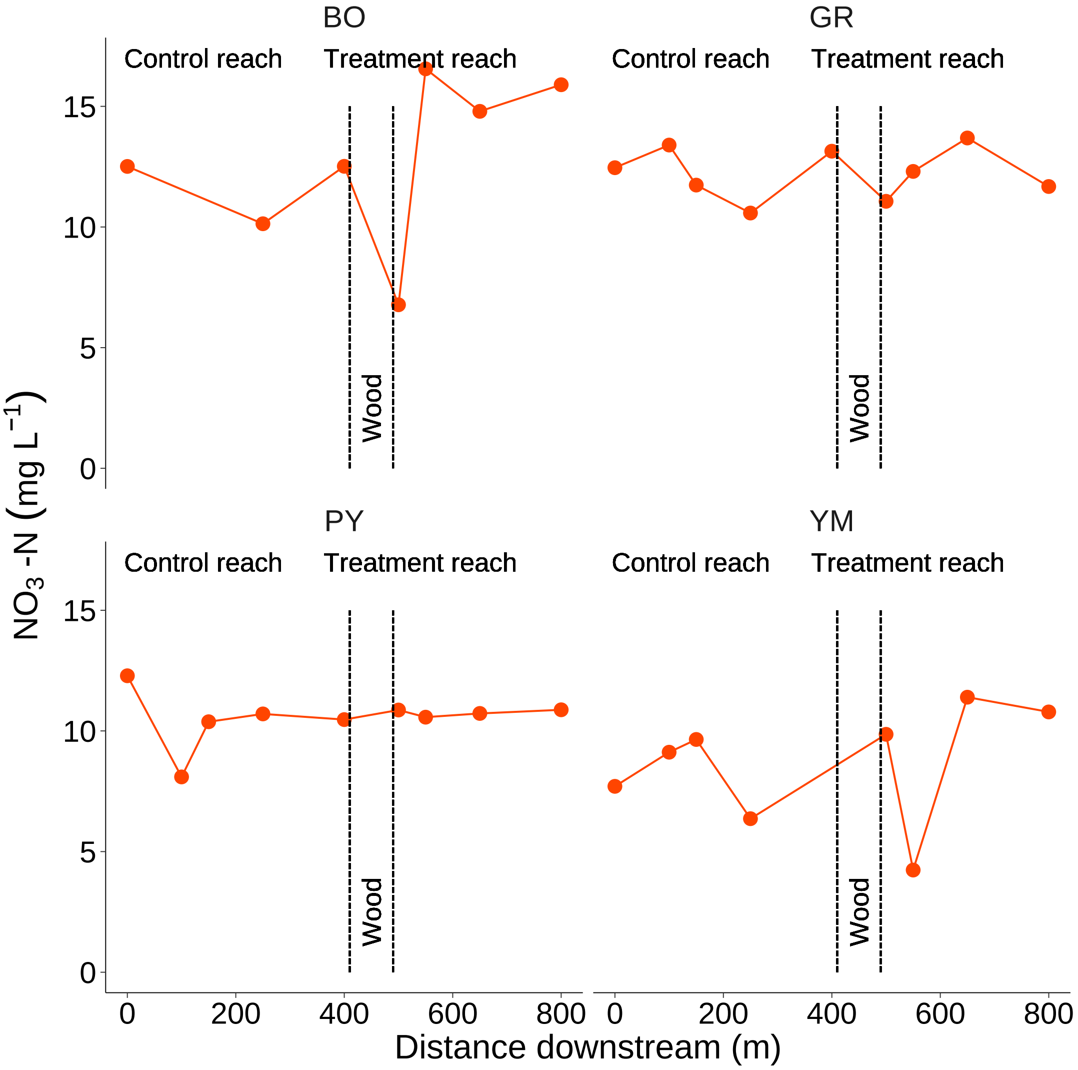

Figure 5.1. Example of nitrate measurements from longitudinally-stratified nutrient sampling in paired control (upstream) and treatment (downstream) reaches for the four-waterway study at the first sampling time ten days after wood was added. Each waterway (two letter codes) is shown in a separate panel. Coloured points are sampling locations within reaches. Dashed lines delineate the 100-m reach where 1.5 m3 pine woodchips (~180 kg dry mass) was added in treatment reaches. We calculated nutrient concentration ranges using the minimum and maximum concentrations within each treatment and control reach for each sampling time.

Statistical analyses

We calculated wood breakdown coefficients (*k*) using an exponential decay model, where the dry mass of wood remaining was log-transformed and regressed versus time (Petersen & Cummins, 1974). We compared wood breakdown in the four treatment reaches within waterways with analysis of covariance (ANCOVA) using linear models (lm) in R (R Core Team, 2016). The response variable was the $\log_e$-transformed dry wood mass (g) remaining, time (days after wood addition) was the covariate, treatment waterway was a fixed factor, and the four waterways were replicates. All data analyses were performed in R version 3.2.4 (R Core Team, 2016).

The goal of our analysis was to detect changes in water column concentrations of nitrate, SRP, and DOC using paired treatment (downstream of wood addition) and control reaches (upstream of wood addition) replicated in four waterways and evaluated on six sampling occasions. We analysed nutrient concentrations, rather than fluxes, since we expected that nutrient concentrations, rather than stream discharge, were more likely to change as a result of the wood addition, given the spring-fed hydrology of these waterways (Chapter Three). We characterised stream nutrient concentration responses within reaches as absolute ranges (maximum – minimum concentration within a reach) of nitrate, SRP, and DOC to encapsulate the fluctuations in concentrations along all sampling points within a reach at a given time (Figure 1). We compared differences in nutrient concentration ranges for each time using the downstream treatment and upstream control reach paired within each waterway to accommodate the potential for key times and locations within reaches where nutrient cycling might be enhanced.

To account for substantial variation in nutrient concentration ranges observed between paired sampling reaches and across waterways over time, and to better represent the influence of our manipulation on biological processes, we analysed treatment effects as effect sizes (Osenberg *et al.*, 1994). Effect sizes were calculated as log ratios: $\log_e$ [control reach nutrient concentration range divided by treatment reach nutrient concentration range]. Using effect size as a response was useful because it had clear ecological meaning and good statistical properties, including an approximately normal sampling distribution (Shurin *et al.*, 2002). Positive effect sizes indicated larger nutrient concentration ranges in control reaches, whereas negative effect sizes corresponded to larger nutrient concentration ranges in treatment reaches. For nitrate-N, SRP, and DOC, negative effect sizes indicated boosted processing in the treatment reach downstream of the wood addition. We calculated means and 90 % confidence intervals for each sampling time using the four waterways as replicates.

For times with significant processing of N in treatment reaches, indicated by negative effect sizes within waterways, we calculated the corresponding reach-level reductions in nitrate concentrations and fluxes. First, we calculated the difference between the minimum concentration observed at the location downstream of the wood and the mean treatment reach nitrate concentration at that time. Using the difference between the minimum and mean concentrations provided a relative reduction in reach nitrate-nitrogen concentrations. Then, we multiplied these relative reductions in mean treatment reach nitrate concentration by the mean treatment reach discharge for each time to determine the relative reduction in treatment reach nitrate flux associated with that distance downstream of the wood. We summarised these overall treatment reductions in nitrate concentrations and fluxes as means and 90 % confidence intervals.

We examined the relationship between the distance downstream of the wood addition (m) and the peak nitrate removal in treatment reaches for times in all waterways where treatment reach effect sizes were less than zero, indicating treatment reach nitrate depletion. Because nutrient data followed a non-linear distribution, were greater than zero, and were not whole numbers (Crawley, 2007), we constructed a generalised linear model with a quasi-poisson distribution using (glm) in R (R Core Team, 2016). To identify the location of maximum N-removal within the treatment reach, we analysed the reach minimum NO_3-N concentration downstream of the wood (m) versus the distance downstream of the wood (m) for the times in each waterway where nitrate effect sizes were negative using linear regression.

Results

The wood addition increased the supply of allochthonous OM in all waterways, with 180 kg of woodchips, equivalent to 1.5 m^3 of submerged wood, added to treatment reaches at the beginning of the experiment. Wood dry mass consistently declined over time, but the rate of wood breakdown differed between waterways indicated by a significant ANCOVA time-by-waterway interaction ($F_{3,8} = 4.29$, $p < 0.05$; Figure 5.2). The wood breakdown rates were low and spanned 0.001 to 0.002 g wood dry mass per day over six months (time: $R^2 = 0.78$, $p < 0.002$). Thus, we substantially increased the amount of allochthonous OM in treatment reaches of all waterways, and wood breakdown was very slow.

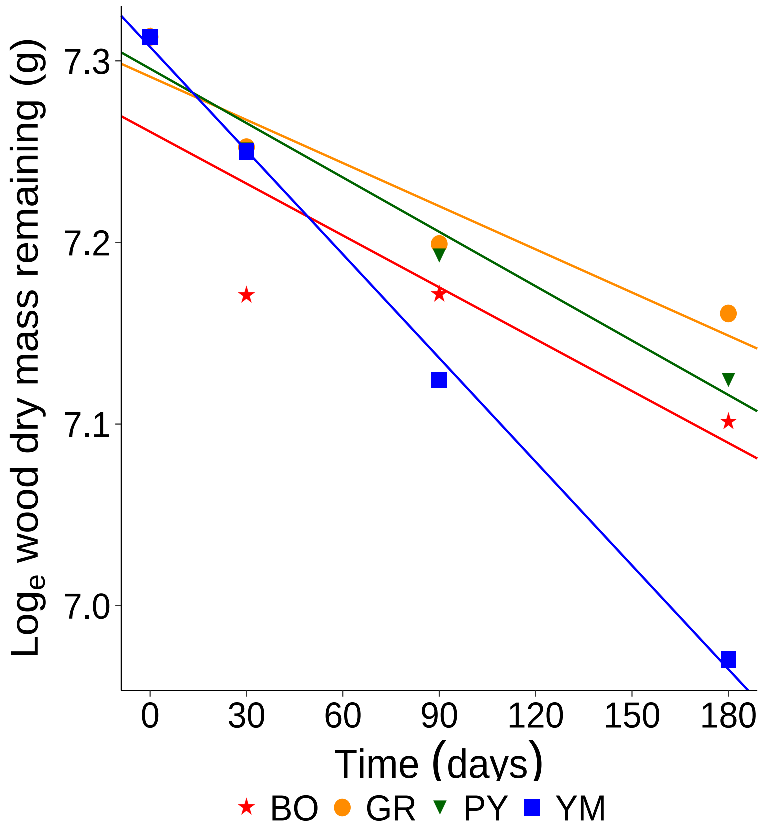

Figure 5.2. Wood breakdown rates from four treatment reaches in agricultural waterways where woodchips were experimentally added in spring 2016. Coloured symbols indicate means from three samples measured per waterway (two letter codes). Coloured lines show significant regressions for each waterway. Note that dry masses were $\log_e$-transformed and the y-axis scale begins at 7.0.

Times and locations with substantial nitrate removal in reaches downstream of the wood addition

Waterway nitrate concentrations were high but varied substantially in all reaches throughout the six-month experiment (mean reach NO_3-N: 8.2 – 17.5 mg L^{-1}). Nitrate concentration ranges measured in treatment reaches downstream of the wood addition tended to be larger than concentration ranges in upstream control reaches at a given time (Figure 5.1). These reach differences in water column nitrate concentration ranges were 4.3 mg NO_3-N L^{-1} higher to 8.4 mg NO_3-N L^{-1} lower in treatment compared to control reaches across all sampling times (Figure S5.1A). Treatment reach nitrate concentration ranges in waterways BO and GR tended to be more consistently larger than in the corresponding control reaches over time, indicated by more consistently-negative effect sizes within these waterways. In comparison, reach nitrate concentration ranges in waterway PY were larger than the corresponding control reach ranges only in the latter half of the experiment (Figure 5.3A). We found marked nitrate processing in treatment reaches relative to control reaches at 10, 33, 110, and 174 days, indicated by negative effect sizes in individual waterways (Figure 5.3A). Overall, we only detected a significant treatment effect, with greater nitrate processing downstream of the wood addition compared to upstream control reaches in all waterways, towards the end of the study (i.e., at 138 and 174 days), indicated by negative effect size means and 90 % confidence intervals that did not overlap zero at these times (Figure 5.3A).

For times when treatment reaches within waterways had greater N processing than the corresponding control reaches, indicated by negative effect sizes, there was no significant relationship in the magnitude of nitrate concentration reductions in treatment reaches and the location downstream of the wood addition ($F_{1,14} = 2.5$, $p = 0.14$; Figure 5.4). Most of the treatment reach nitrate removal occurred 5 – 50 m downstream of the wood addition, but also up to 300 m downstream (Figure 5.4). Overall, adding in-stream wood did influence treatment reach nitrate removal, but only sporadically initially, and with peak nitrate removal occurring at different times and locations across streams. This treatment effect of greater depleted reach nitrate concentrations downstream of the wood addition became more consistent over time, and it was occurring consistently in all waterways approximately five and six months after wood was added.

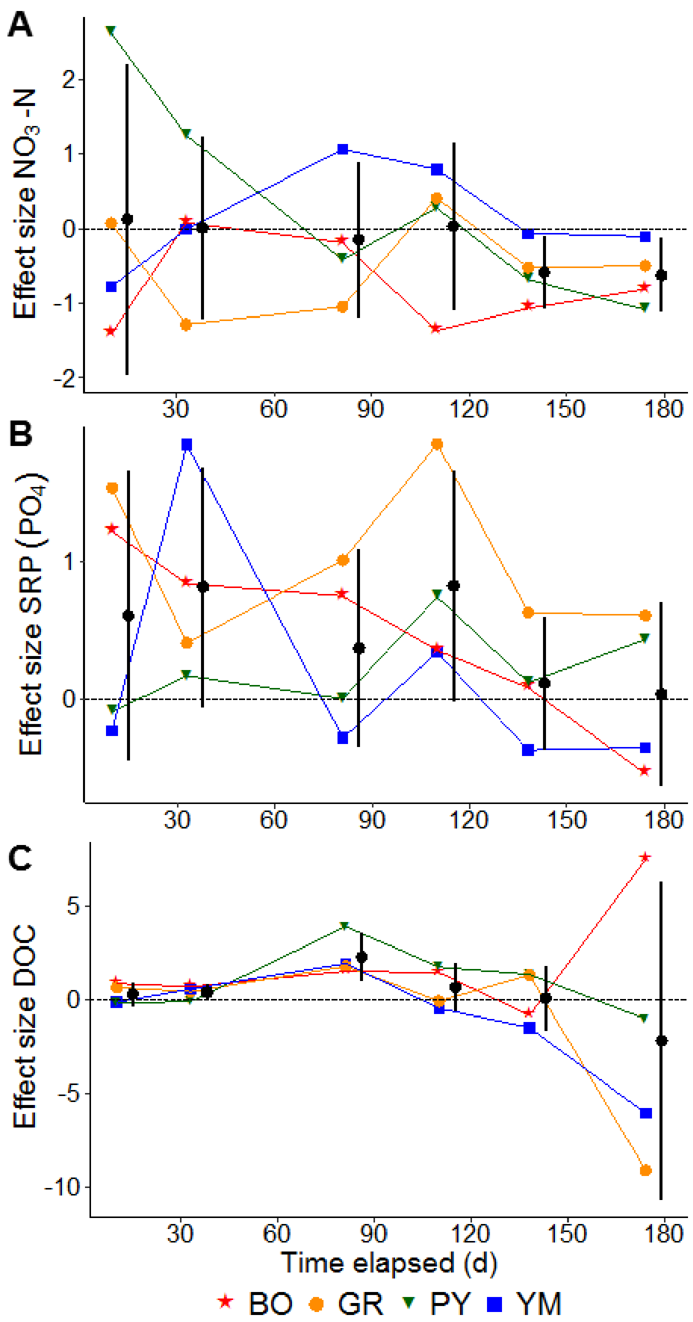

Figure 5.3 Effect sizes ($\log_e$ control reach concentration range divided by treatment reach concentration range) for (A) nitrate-nitrogen, (B) soluble reactive phosphorus (SRP, phosphate), and (C) dissolved organic carbon (DOC) calculated for each sampling time within each waterway post-wood addition. Coloured symbols and lines correspond to sampling times within each waterway (two letter codes). Black dots and whiskers show effect size means +/- 90% confidence intervals for the four waterways at each sampling time. Dashed lines intercepting y=0 indicate no net change in nutrient concentrations between upstream (control) and downstream (treatment) reaches. Positive effect sizes correspond to greater processing in upstream control reaches, and negative effect sizes correspond to greater processing in the treatment reaches downstream of the wood addition.

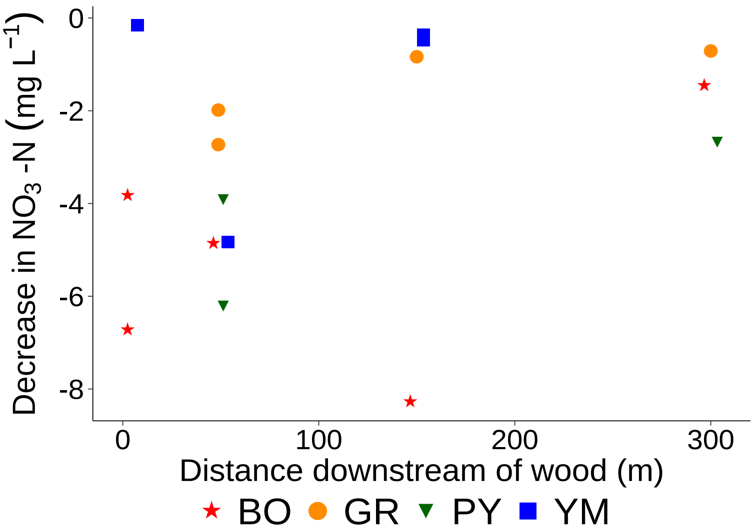

Figure 5.4 Locations of decreases in nitrate concentrations in treatment reaches downstream of the wood addition for times indicated by nitrate effect sizes less than zero in each waterway. Coloured symbols indicate different waterways (two-letter codes).

Patterns of SRP and DOC retention or removal in reaches downstream of the wood addition

We anticipated that SRP concentrations would be variable in reaches, reflecting the inherent variability in ecosystem processes that are influenced by some combination of C, N, and P availability. Compared to nitrate, mean SRP concentrations remained low and varied less in all reaches over the duration of the experiment (mean reach PO_4: 0.8 – 17.3 μg L^{-1}; Figure S5.2A). However, the differences in water column SRP concentration ranges between paired reaches were between 6.4 μg L^{-1} PO_4 lower in treatment reaches to 1.7 μg L^{-1} PO_4 higher in treatment reaches. Examining the effect sizes of reach SRP ranges revealed that overall, control reaches often had higher SRP than treatment reaches, indicated by positive effect sizes for individual waterways (Figure 5.3B). Waterway YM was the only waterway where the treatment reach downstream of the wood tended to have more SRP than the upstream control reach, indicated by negative effect sizes (Figure 5.3B). Across all waterways, control reach SRP was significantly higher at 110 days, indicated by a 90 % confidence interval that did not overlap zero (Figure 5.3B). Thus, although SRP concentrations remained low in all waterways, we often found less SRP in reaches downstream of the wood addition compared to upstream control reaches, but the effect was mostly inconsistent across waterways.

Similar to SRP, mean DOC concentrations were low in all reaches during the experiment (mean reach DOC: < 0.01 – 8.5 mg L^{-1}; Figure S5.2B). The differences in water column DOC concentration ranges within waterways were between 30.5 mg L^{-1} lower in treatment reaches to 7.5 mg L^{-1} higher DOC in treatment reaches. Examining the effect sizes of reach DOC concentration ranges revealed that control reaches had significantly higher DOC than treatment reaches during the first half of the experiment at 10, 33 and 81 days, indicated by 90 % confidence intervals that do not overlap zero (Figure 5.3C). However, unlike patterns in nitrate or SRP, DOC concentrations changed more consistently across waterways over time, with a strong increase in DOC in treatment reaches downstream of the wood in all waterways, except BO, on the last sampling occasion, ~6 months after the wood addition (Figure 5.3C).

Discussion

Ecosystem-level C imbalances in small agricultural waterways can limit their ability to cycle nutrients (Stutter *et al.*, 2018). Consequentially, these waterways with limited nutrient cycling can disproportionately influence downstream nutrient loads and ecosystem functioning by being net sources rather than sinks of nutrients (Alexander *et al.*, 2007; Woodward *et al.*, 2012). Nutrient cycling in agricultural headwaters can be characterised by high retention or cycling, but nutrient uptake is often saturated by high nutrient inputs, limited by low organic matter and DOC, and constrained by low in-channel structural complexity to retain and process organic matter and nutrients (Craig *et al.*, 2008; Stutter *et al.*, 2018). Managing the supply of in-stream wood is likely important to boost terrestrial OM, and stimulate nutrient removal and retention (Collier & Bowman, 2003; Entrekin *et al.*, 2008; Elosegi *et al.*, 2016). However, little is known about how agricultural waterways with severe nutrient imbalances may respond to rehabilitation with organic matter or DOC amendments, despite organic matter additions being an increasingly important management tool (Faust *et al.*, 2016; Stutter *et al.*, 2018). We tested experimental additions of in-stream wood (pine woodchips) to enhance N and P removal in spring-fed agricultural headwaters with low terrestrial OC stocks and high nitrate inputs from groundwater. Our waterways were C-limited, indicated by C:N ratios outside of the microbial flexible zone for river nutrients (Stutter *et al.*, 2018). Under these C-limiting conditions, N likely becomes saturated and decoupled from N cycling (Stutter *et al.*, 2018). Adding in-stream wood produced highly variable patterns of nitrate removal, with nitrate removal differing substantially within experimental and control reaches and over time. Overall, our wood only consistently stimulated removal and retention of nitrate towards the end of the experiment, five to six months after wood addition. Our results highlight the ecological importance of increasing terrestrial OM supply in agricultural waterways to attenuate downstream nutrients by illustrating what might be possible, but also highlighting the substantial challenges left to face in achieving enhanced N attenuation consistently.

Evaluating the outcomes of stream rehabilitation is not straight-forward, since nutrient concentrations can fluctuate dynamically with source water inputs along waterways (e.g., groundwater, surface runoff, and subsurface drainage water) that also change over time (Yanai *et al.*, 2015; Williams *et al.*, 2015d), consistent with the ecosystem control points paradigm (Bernhardt *et al.*, 2017). Our experimental additions of in-stream OM likely enhanced ecosystem control points of nutrient retention and removal, which were manifested as highly dynamic locations in treatment reaches downstream of the wood over different times during the experiment. Importantly, concentrations were fairly variable in both control and treatment reaches, highlighting the importance of evaluating ecosystem ecology across larger spatial scales and over time to detect ecologically important changes due to stream rehabilitation (Filoso & Palmer, 2011). The ecological inference gained from post-implementation assessments of rehabilitation is often constrained by monitoring at insufficient spatial or temporal scales, as well as the substantial environmental variability that clouds detection of responses to rehabilitation actions (Palmer *et al.*, 2005, 2014). Here, characterising the variability in nutrient concentrations was more instructive than using mass-balance approaches measuring only the 'ins and outs' at a set time (Yanai *et al.*, 2015; Williams *et al.*, 2015d). For example, nine of the sixteen times with substantial reductions in treatment reach nitrate flux (i.e., when nitrate concentration effect sizes were less than zero for individual waterways) occurred 5 – 50 m downstream of the wood addition. However, there was no consistent relationship of where these were located within the treatment reach downstream of the wood addition. Hence, water is likely to have travelled downstream from where the actual control point of enhanced nutrient cycling occurred.

Our study is one of the first to demonstrate that wood addition could potentially stimulate nutrient attenuation in agricultural headwaters with chronically high (saturated) nitrate and limited terrestrial OM. However, attenuating high in-stream N was not as simple as just adding OM, which did not consistently enhance nutrient removal downstream of the wood or over time. Averaging across the times in each waterway when treatment reach nitrate concentrations were lower than in control reaches, indicated by nitrate concentration effect sizes less than zero, treatment reach water column nitrate concentrations were lower than the mean reach concentration by an average of 3.0 mg L^{-1} NO_3-N (90% CI: 2.5 – 3.5 mg L^{-1} NO_3-N). These treatment concentration reductions potentially correspond to average reductions in treatment reach nitrate fluxes of 10.0 kg d^{-1} NO_3-N, equivalent to 24.2 % reductions in the mean treatment reach nitrate load (90% CI: 20.1 % – 28.08 %) at those times. However, substantial diffuse nitrate inputs downstream from the wood (e.g., from springs or upstream sources) or nitrification likely obscured any wood effect along the rest of the reach. Hence, reach nitrate levels increased again further downstream. Therefore, considering how the nitrate removal control points created by the wood additions and reach-scale groundwater inputs interacted was key to evaluating the overall effects of stream rehabilitation to reduce downstream nitrate concentrations and fluxes. We extended the application of the ecosystem control points paradigm by not only characterizing the underlying spatial and temporal dynamics of N attenuation, but also by revealing what might be possible by overcoming carbon limitation at larger scales within catchments.

The substantial decreases in nitrate downstream of our wood addition illustrate what might be possible by boosting in-stream OM to overcome carbon limitation in these waterways. However, given that catchment-scale degradation often limits stream restoration efforts at the reach-scale (Bernhardt & Palmer, 2011), process-based rehabilitation will likely be necessary to procure more consistent nutrient attenuation throughout the stream network. Given the influences of catchment hydrology, waterway channelization, and the lack of in-stream structures to promote contact with the benthos and retain OM, rehabilitation approaches that boost, re-connect, and retain terrestrial OM in riparian buffers, floodplains, and in-stream may enhance catchment nutrient attenuation (Lammers & Bledsoe, 2017; O'Brien *et al.*, 2017; Hanrahan *et al.*, 2018). Matching or 'stacking' multiple tools across these influential locations along the stream network is a potentially effectual, yet underutilized rehabilitation approach that could enhance nutrient retention and removal (Chapter Four). Furthermore, assessing how nutrient removal and retention might be enhanced by rehabilitation actions likely requires an ecosystems-approach to account for the complex interactions of nutrient stocks and stream ecosystem processes (Palmer & Febria, 2012).

Surprisingly, few stream nutrient cycling studies examine concurrent changes in N, P, and DOC, despite the important linkages of these macronutrients on microbially-mediated nutrient cycling and OM decomposition (Newcomer Johnson *et al.*, 2016; Glibert, 2017). Our findings contribute to a small, but growing number of studies showing that alleviating carbon limitation by boosting in-stream organic matter stocks can enhance nutrient removal (Fork & Heffernan, 2014; Waters *et al.*, 2014; O'Brien *et al.*, 2017). Intensive agricultural land-use and multiple-stressor effects can confound patterns in organic matter breakdown and other ecosystem processes related to stream metabolism and nutrient cycling (Hagen, Webster & Benfield, 2006; Tank *et al.*, 2010). Interestingly, nitrate decreases did not co-occur with increases in DOC in treatment reaches, as was observed within six months of in-stream *Pinus radiata* manipulation in spring-fed, forested headwater streams (Collier & Bowman, 2003). Therefore, our wood addition likely stimulated N removal through uptake as well as denitrification, since DOC and SRP were also lower in treatment reaches relative to controls. Moreover, the breakdown rates of wood in our waterways was somewhat faster than the breakdown rate of *Pinus* spp. reported in other studies (Collier & Smith, 2003; Spänhoff & Gessner, 2004; Meleason & Hall, 2005), which may have contributed to the relative increase in treatment reach DOC concentrations in three of the four waterways after six months. The wood likely increased nutrient retention and removal by providing a substrate for microbes, and these in turn increased the uptake and assimilation of N, P, and DOC. Thus, measuring ecosystem process such as denitrification, stream metabolism, and organic matter breakdown are likely to further elucidate the organic matter cycling pathways (Tank *et al.*, 2010). Overall, evaluating multiple ecosystem processes at multiple locations and times should help disentangle the benefits of stream rehabilitation on restoring key ecosystem functions (Palmer & Febria, 2012).

In conclusion, we found good prospects for enhancing nitrate retention and removal with stream rehabilitation tools in small, agricultural waterways that receive considerable nitrate inputs during base flows offer, since denitrification in these waterways is more likely to be limited by C than N (Arango *et al.*, 2007; Littlejohn *et al.*, 2014). Our findings underpin the importance of relating OM stocks, DOC dynamics, and how these impact nutrient uptake to inform nutrient management and rehabilitation tools in agricultural waterways (Stanley *et al.*, 2012). Considering the substantial fluctuations in nutrient inputs, DOC supply, and the overwhelming influence of high spring/upstream source water nitrate on governing downstream N loads in these waterways, the variable and sometimes significant reductions in nitrate concentrations provided surprising evidence that simple stream rehabilitation tools implemented at larger scales (reaches) can influence stream ecosystem functioning, even in nitrate-saturated agricultural waterways. However, procuring more consistent downstream nutrient attenuation will likely require combining process-based rehabilitation at multiple locations throughout the stream network (Lammers & Bledsoe, 2017). The challenge of targeting, combining, and scaling-up efforts to improve how these waterways can attenuate nutrients will require concerted efforts from scientists, practitioners, farmers, and other landowners (David *et al.*, 2015). Future evaluations of stream rehabilitation to enhance nutrient attenuation should adopt an ecosystems approach, whereby multiple indicators of ecosystem functioning, such as nutrient cycling, organic matter breakdown, and stream metabolism, are assessed over key times at impactful spatial scales (i.e., reaches and catchments).

Supplement to Chapter Five

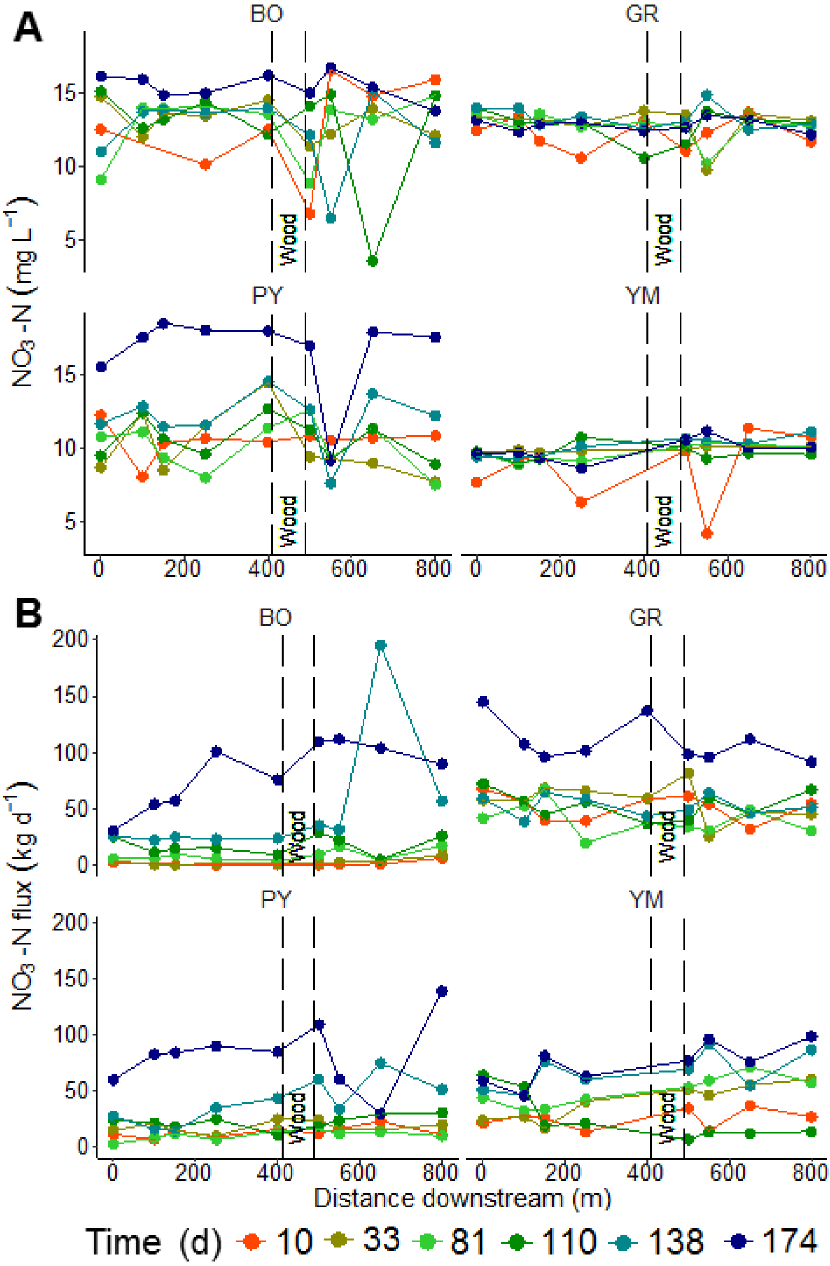

Figure S5.1 Longitudinal nutrient sampling data in paired control and treatment reaches over time for (A) nitrate-nitrogen (mg L^{-1}) and (B) nitrate-nitrogen fluxes (kg d^{-1}). Points correspond to sampling locations measured repeatedly (different colours) during the experiment (days since wood addition). Waterways (two-letter codes) are shown in separate panels in each plot. Dashed vertical lines delineate the wood addition locations. Sampling points upstream of the wood were control reaches, and sampling points including and downstream of the wood were treatment reaches.

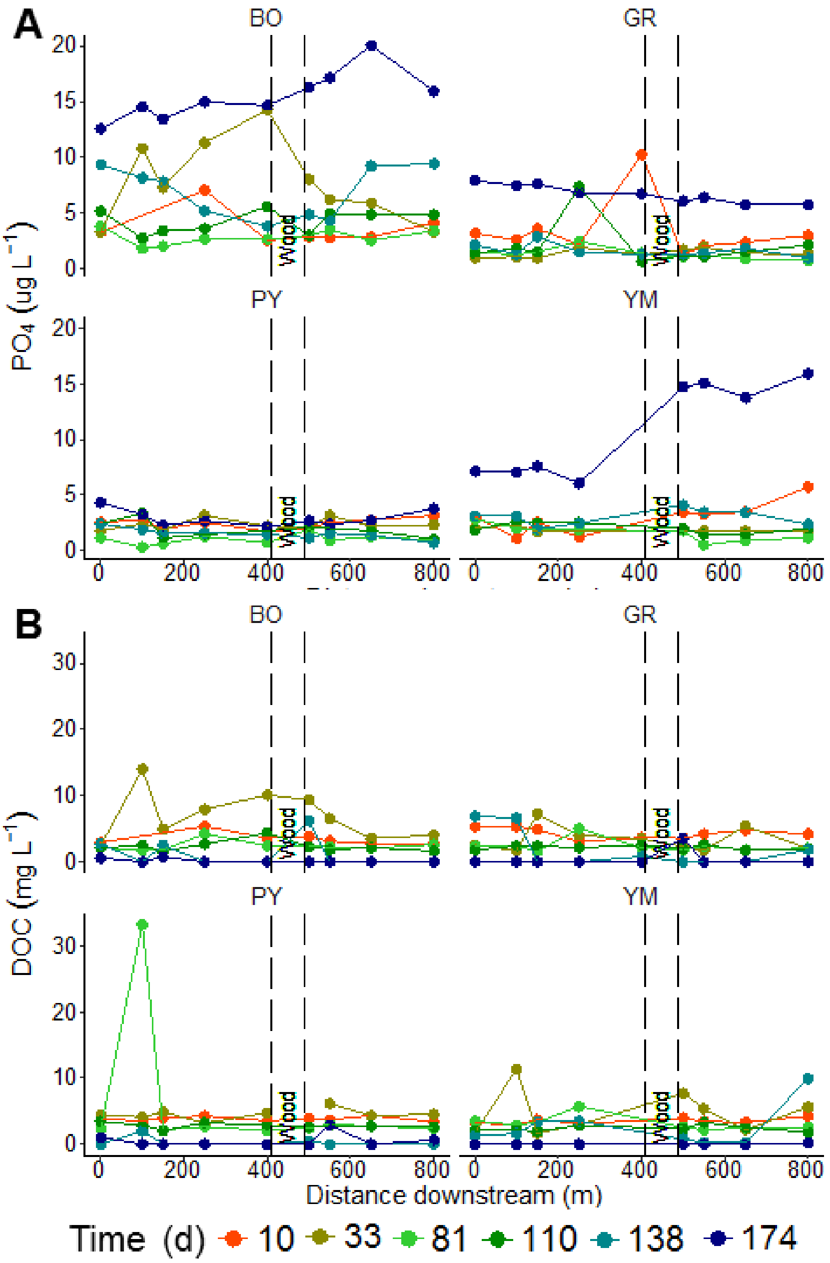

Figure S5.2. Longitudinal nutrient sampling data in paired control and treatment reaches over time for (A) soluble reactive phosphorus (phosphate, µg L^{-1}) and (B) dissolved organic carbon (DOC, mg L^{-1}). Points correspond to sampling locations measured repeatedly (different colours) during the experiment (days since wood addition). Waterways (two-letter codes) are shown in separate panels in each plot. Dashed vertical lines delineate the wood addition locations. Sampling points upstream of the wood were control reaches, and sampling points including and downstream of the wood were treatment reaches.

Plate 6. Additional riparian planting filling in the gaps along a rehabilitated agricultural waterway, with view of Mount Hutt on the Canterbury Plains

Photo: Hayley S. Devlin

Chapter Six:

Synthesizing stream nutrient attenuation and rehabilitation insights to improve agricultural waterway management

Drainage ditches and small streams are often the headwaters of many agricultural catchments worldwide (Blann *et al.*, 2009). These small waterways can disproportionately influence downstream nutrient loads, nutrient cycling, and ecosystem processes in receiving rivers (Dodds & Oakes, 2008; Woodward *et al.*, 2012). Given the need to meet anthropogenic food, fibre, and fuel demands while also managing human and ecosystem health in these waterways, improved agricultural nutrient management practices and stream rehabilitation approaches are urgently needed (Pretty *et al.*, 2010; Lammers & Bledsoe, 2017). Nutrient attenuation and rehabilitation tools can enhance reactive nitrogen (N) and phosphorus (P) removal and retention along and within these waterways (Lammers & Bledsoe, 2017; Mander *et al.*, 2017). However, managers and practitioners need better information to disentangle and target the contributions of farm- and catchment-scale nutrient inputs to downstream nutrient loads. Furthermore, evidence is needed to show how rehabilitation interventions at different locations along the stream network might attenuate excess nutrients downstream (Filoso & Palmer, 2011; Christianson *et al.*, 2014). I undertook this research as part of the Canterbury Waterway Rehabilitation Experiment (CAREX) in agricultural, headwater waterways to: 1) characterize the hydrological and catchment-scale drivers of stream nitrate loads, 2) implement nitrate removal tools targeting the key nutrient sources and their scales along the stream network, and 3) evaluate the in-stream and ecosystem-level impacts. In this chapter, I synthesize the key insights generated by my research to address and improve stream nutrient attenuation and rehabilitation strategies in agricultural catchments.

Key insight 1: Contextualise the scales and sources of nutrient inputs to guide management and stream rehabilitation

Characterising the spatial and temporal variability in waterway nutrient loads and understanding how these change across and within agricultural catchments provides a fundamental basis for improving nutrient management and stream rehabilitation (Abbott *et al.*, 2017; McDowell *et al.*, 2017). However, characterising nutrient fluxes in these waterways with variable hydrology and nutrient export can be very challenging and sampling-intensive (Harmel *et al.*, 2006; Williams *et al.*, 2015d). The dynamic patterns in nutrient fluxes that change with land management and waterway connectivity are nefarious obstacles to management (Royer *et al.*, 2006; Baker *et al.*, 2008). Furthermore, these nutrient fluxes can change with different sources of nutrient inputs along the stream network from surface run-off, groundwater, riparian seeps, subsurface tile drains, and open tributary drains (King *et al.*, 2014; Williams *et al.*, 2015a b). I conducted one of the only replicated, multi-year assessments of agricultural headwater catchment nitrate loads available in the literature, and in doing so, I quantified the seasonal and catchment-scale drivers of nitrate export (Chapter Three). By revealing the influences of increased base flows in wet seasons, high groundwater nitrate inputs from upstream sources, and the relative contributions of tributaries (i.e., subsurface tile and open drains), I provided a basis to inform the design and importantly the locations of stream rehabilitation tools to attenuate catchment nitrate.

By testing the relative contributions of nitrate inputs along a stream network, I revealed that the current, predominant Canterbury nitrate management practice of stock exclusion from waterways by fencing is insufficient to reduce the high loads driven by groundwater (Chapter Three). Identifying and managing for the loads, times, and locations where excess nutrients are transmitted to waterways (e.g., legacy nutrients from groundwater or stream sediments, subsurface drainage, etc.) provides a template for management and rehabilitation actions. Stream rehabilitation practitioners can use the knowledge of these nutrient sources and their delivery pathways to design rehabilitation programmes that optimise farm- and catchment-scale nutrient attenuation. High groundwater nitrate inputs may be lowered by improved farm management practices, e.g., fertiliser management, and these are especially important in regions like Canterbury with limited nitrate denitrification in groundwater (Di & Cameron, 2002; Rivett *et al.*, 2008). However, high groundwater nitrate fluxes to waterways will likely continue to be problematic due to the long travel and lag times in groundwater and the pollution legacy from what is often termed the 'load to come' (Schiel & Howard-Williams, 2016). In light of the need to continue farming and to deal with nutrient pollution legacies, the results presented in my thesis support the implementation of combinations of stream rehabilitation tools to attenuate catchment nutrient loads. The substantial nitrate fluxes from upstream springs, in combination with those from tile and open tributary drains, should be targeted for management at the farm-scale to complement catchment-scale and land-based nitrate attenuation measures and requires further testing/trialling at these scales.

Key insight 2: Waterway nutrient management and rehabilitation actions can be optimised by implementing sets of different tools to target multiple nutrient inputs at multiple scales

A variety of nitrate-removal tools can be implemented to intercept nutrients from key pathways and enhance nutrient cycling at multiple locations along and within the stream network (Craig *et al.*, 2008; Newcomer Johnson *et al.*, 2016; Faust *et al.*, 2017). These tools can be implemented at the edge-of-field, in riparian buffers/floodplains, within the channel margins, and in-stream (Table 6.1). Nitrate attenuation and rehabilitation tools enhance nutrient retention and removal through similar mechanisms, including increasing water retention, promoting contact with the benthos, and providing organic matter and carbon source (Table 6.1); therefore, it would seem advantageous to combine or 'stack' multiple tools to create additive effects by enhancing the key nitrate removal mechanisms with different tools. Nevertheless, despite the need to address catchment nutrient loads at the reach-, farm-, and catchment-scales, nitrate-removal tools are rarely implemented in a complementary way that combines different tools targeted across these influential scales (Kröger *et al.*, 2015; Weigelhofer, Hein & Bondar-Kunze, 2018). My research looked at multiple N-removal tools and showed that it might be possible to reduce contaminants such as nitrate by implementing replicates of tools. For example, while a single bioreactor may remove a substantial portion of the N load from a single edge-of-field source, multiple bioreactors along a catchment may concertedly reduce downstream N export (Chapter Four). However, implementation of these tools may cause some interference with agricultural production, drainage provision, and drain maintenance. Hence, striving to provide optimal environmental improvements to agricultural waterways with rehabilitation in working landscapes will likely require compromises from landowners. Within the CAREX project, we developed a fit-for-purpose nitrate-removal 'toolbox' and public demonstration sites that feature a range of evidence-based options with compromises that farmers accepted or were feasible to reduce catchment nutrient loads. When implementing nitrate-removal tools from this stream nutrient rehabilitation toolbox, the suitability of measures must be considered, based on: space/land requirements, cost-effectiveness, social acceptability/compromises, and the anticipated physicochemical, hydromorphological, and ecological outcomes (Beechie *et al.*, 2008; Bernhardt & Palmer, 2011; Hermoso *et al.*, 2012).

I added to the growing body of evidence that underscores the importance of rehabilitating riparian buffers and in-stream nutrient cycling to enhance nutrient removal through multiple pathways across a range of waterway hydrology and nitrate fluxes (Ranalli & Macalady, 2010; Newcomer Johnson *et al.*, 2016). My research generated new knowledge around rehabilitation ‘tool matching’ in a Canterbury context, where different nitrate-removal tools were implemented at key locations or ‘control points’ (*sensu* Bernhardt *et al.*, 2017) along and within the stream network to attenuate catchment nitrate export (Chapters Four and Five). This multiple-tool, multiple-scale toolbox approach quantified how downstream water quality can be improved through both the establishment of riparian protection systems and scale- and source-matched N-removal tools – edge-of-field woodchip bioreactors and in-stream additions of small wood. Implementing different tools at complementary scales along and within the stream network accrued benefits to downstream water quality and ecosystem functioning. For example, enhancing riparian nutrient cycling boosts in-stream nutrient retention and removal by filtering fine sediment and nutrients from run-off and subsurface flows (Ranalli & Macalady, 2010; Lammers & Bledsoe, 2017). Additionally, riparian vegetation can provide a source of organic matter and shading to mitigate in-stream eutrophication (Burrell *et al.*, 2014; Halliday *et al.*, 2016; O’Brien *et al.*, 2017). Although riparian planting is a common waterway rehabilitation tool (McKergow *et al.*, 2016), I showed that this tool alone is not enough to attenuate catchment nitrate loads. My results underscore the importance for practitioners to ‘think outside the box’ by implementing and evaluating additional nutrient removal tools and practices at multiple influential locations to reduce waterway nutrient loads (Table 6.1). Adopting a toolbox-based stream rehabilitation approach that stacks multiple, different tools along and within the stream network may enhance the benefits provided by riparian buffers and other tools (Stutter *et al.*, 2012; Zak *et al.*, 2018) can help overcome factors that limit nutrient removal and retention in small, agriculturally-impacted waterways.

Table 6.1 Overview of nitrate attenuation tools suitable for agricultural waterways and the mechanisms for nitrate removal. Tools are grouped by their location from the edge-of-field to in-stream. The mechanisms for nitrate removal are based on Craig et al. (2008).

Location	Rehabilitation tool	Increases water residence / retention time (contact with benthos)	Enhances groundwater-surface water exchange (contact with benthos)	Increase surface area-to-volume ratio (contact with benthos)	Promotes removal via contact with vegetation and organic soils	Enhances conditions for denitrification
Edge-of-field	Redirect subsurface drainage (e.g., controlled drainage)	x	x		x	x
	Store water (e.g., retention / detention buns)	x	x		x	
	Install tile drain or 'wet spot' bioreactors*	x				x
Riparian buffer / floodplain	Reconnect floodplain / re-shape stream banks*	x		x	x	x
	Modify flow paths (e.g. side channels, ponds/wetlands)	x	x		x	x
	Plant riparian buffer*				x	x
Within channel margins	Create meander bends	x	x	x		
	Create in-set floodplains (e.g., two-stage channels) *	x		x	x	x
	Widen channel	x		x		
In-stream	Add in-stream geomorphic features (e.g., boulders) *	x	x			
	Install debris dams / low-grade weirs	x	x			x
	Add large woody debris	x	x			x
	Organic matter addition (e.g., leaves, small wood) *	x				x
	Install in-stream bioreactors*	x				x

*Rehabilitation tool trialled within CAREX

Key insight 3: Overcoming limiting factors to implement riparian and in-stream nutrient rehabilitation

Changes in the hydrology and water chemistry of edge-of-field and in-stream nutrient inputs can greatly influence the performance of nitrate attenuation tools (Goeller *et al.*, 2016). Another considerable challenge in rehabilitating the intrinsic ability of agricultural waterways to cycle nutrients is to overcome carbon (C) limitation, since organic matter stocks and supply are often insufficient relative to the high excess N and P (Stutter *et al.*, 2018). Given the dynamic nature of how hydrology, abiotic conditions, and C supplies can influence N attenuation, functionally-based rehabilitation approaches are needed to overcome these limiting factors. Because hydrological variability drove waterway nitrate fluxes and influenced the performance of nitrate-removal tools, accounting for these influences on catchment nitrate loads was prerequisite to making our stream rehabilitation effective (Chapters Three and Four). My research has improved our understanding of how simple and pragmatic rehabilitation tools implemented at key locations in the stream network can reduce downstream nutrient fluxes, despite highly variable source water chemistry and hydrology. In spring-fed waterways, or where base flows dominate nutrient export, my results emphasise that functionally-based stream rehabilitation should increase in-stream hydraulic residence time (HRT) and enhance the standing stock of organic matter to effectively boost stream nutrient removal and retention. Suitable nitrate-removal options for these waterways could include saturated riparian buffers, variable width riparian buffers, low-grade weirs, or meanders to increase HRT and organic matter retention (Table 6.1). In other regions where waterways have flashier or surface runoff-dominated hydrology, functionally-based stream rehabilitation may need to involve a suite of tools designed to collect and intercept surface runoff, such as water detention or retention structures and controlled drainage, or increase HRT and contact with the benthos across the stream channel, e.g., with in-set floodplains or low-head weirs. By combining multiple tools to overcome the factors that limit the inherent ability of waterways to attenuate nutrients, small agricultural waterways impacted by multiple stressors can behave more like linear wetlands (Soana *et al.*, 2017; Schilling *et al.*, 2018), potentially providing greater ecosystem benefits than channelized ditches primarily intended to drain water from the landscape.

Key insight 4: Think holistically about the impacts of nitrate loss enhancement tools on ecosystem ecology and apply an ecosystems approach to managing nitrogen

While evaluating the performance of individual nitrate-loss enhancement tools at a particular source is important, my research informed nutrient management strategies by elucidating the overall impacts of a combination of tools on reducing downstream nitrate loads and rehabilitating ecosystem functions. Excess reactive N and P can influence several key ecosystem functions linked to ecosystem health (Stokstad, 2005; Rockström *et al.*, 2009). Because ecosystem process may be affected differently by excess nutrients, there is no consensus on which indicators best capture ecosystem health (Palmer & Febria, 2012). Hence, although small waterways with consistently high nutrient inputs may provide good opportunities for implementing stream rehabilitation (Craig *et al.*, 2008), the response of these ecosystems to rehabilitation actions may not be immediate or obvious to detect (Filoso & Palmer, 2011). Therefore, I synthesized a protocol using the linkages among bioreactor performance criteria, stream health indicators, and waterway monitoring locations to establish a starting point for practitioners to incorporate stream ecology into edge-of-field nitrate management (Goeller *et al.*, 2016). Furthermore, the timing of sampling and the suite of water quality and ecosystem health indicators evaluated influence how we contextualise the impacts of waterway nutrient rehabilitation (Goeller *et al.*, 2016). For example, a mass-balance approach by monitoring the 'ins and outs' was inadequate to detect changes in nutrient fluxes associated with riparian and in-stream nutrient rehabilitation tools (Chapters Four and Five). Rather, capturing these variable dynamics required sampling in multiple locations over time and using a robust before-after-control-impact (BACI) experimental design, which is unfortunately not an approach used in most stream rehabilitation projects (Bernhardt *et al.*, 2005; Palmer *et al.*, 2005). Within the CAREX project, we measured a suite of hydro-physical, nutrient, biological, and ecosystem responses over multiple spatial and temporal scales. Integrating and contextualising the information on how indicators of ecosystem health, such as organic matter breakdown, nutrient cycling, greenhouse gas (GHG) production, stream metabolism, and invertebrate foodweb structure respond to stream rehabilitation will provide managers with a bigger picture of how the structure and function of waterways changes due to management actions.

Integrated, whole-ecosystem, evaluations of nutrient-loss and stream rehabilitation tools are needed to disentangle how nitrate removal tools are linked to stream ecosystem processes. For example, organic matter breakdown, nutrient flow, ecosystem respiration, and gross primary productivity are affected by stream hydrology, fine sediment inputs, and nutrient loads (Goeller *et al.*, 2016). Given that different nutrient-removal tools provide unique suites of environmental benefits and ecosystem services (Christianson *et al.*, 2014), stream rehabilitation practitioners should benchmark and evaluate the outcomes and interactions of farm-scale nutrient attenuation within a catchment-context using combinations of multiple, different tools. In particular, future assessments of the ecosystem-level impacts of nutrient-loss enhancement tools should consider the potential impacts and trade-offs on: nutrient retention and removal, water quality, ‘pollution swapping’ and GHG emissions, chemical/biological oxygen demand, or phosphorus release (Goeller *et al.*, 2016). In light of these complex ecosystem feedbacks, it seems advantageous that stream rehabilitation should be conducted through collaborations with a range of experts, practitioners, and landowners. A major feature of my research and the overall CAREX approach to stream rehabilitation was working collaboratively to disentangle the complex responses of stream ecosystems to our pragmatic rehabilitation tools.

Key insight 5: Ecosystem rehabilitation requires a team effort – work collaboratively, share knowledge, and embrace adaptive management

Real-world solutions for reducing catchment nutrient loads must fit into working farms and landscapes; therefore, the people and the place (local social and cultural context) should also influence stream rehabilitation actions (Lawson *et al.*, 2017). An essential element of my research and the CAREX project were the key partnerships and long-term commitments built among scientific experts, practitioners, policy makers, and landowners. From project inception to completion, actively engaging and co-designing/developing trials with farmers and communicating our research outcomes to these and other key stakeholders enriched the science and practice of our stream rehabilitation. For example, walking along the waterways with landowners and discussing farm and stream management issues revealed shared opportunities to jointly improve these, e.g., by varying fenced buffer widths to encompass slumps and rills in pastures, using additional riparian plantings to fill in gaps, or implementing bioreactors at problematic wet spots at the edge-of-field. These partnerships and outreach demonstrated the effectiveness of 'translational ecology' in practice (Jackson, Garfin & Enquist, 2017). From January 2014 to March 2018, the CAREX team reached out to over 2900 people via presentations, outreach events, workshops, and newsletters. Some of the farthest-reaching outcomes of my research were the stakeholder-driven science communication and translational ecology that I contributed to, including: stream rehabilitation fact sheets, farm visits, news articles, presentations to local/regional governments and research agencies, as well as scientific publications and conference presentations (Figure 6.1). Importantly, discussing both the successes and failures of the stream rehabilitation tools and methods trialled were essential for adaptive management locally. Overall, the collaborative, inclusive process we used to shape and disseminate our stream rehabilitation programme was vital to enhancing its uptake and the potential to transform decision making to improve ecosystem nutrient management in agricultural landscapes.

In conclusion, I found no silver bullet for solving nutrient problems in agricultural waterways. Rather, my research was part of a larger effort that demonstrated that effective stream rehabilitation required a coordinated partnership with multiple stakeholders, especially landowners, to strategically implement stream rehabilitation tools targeting multiple stressors at their influential scales along and within the stream network. Stream rehabilitation projects conducted within different landscape contexts should be treated as adaptive management experiments rather than solutions to nutrient loading issues, while better data on the catchment- and ecosystem-level impacts of rehabilitation actions is obtained (David *et al.*, 2015). Using a data-driven adaptive management approach, riparian and in-stream rehabilitation programmes can then be scaled up accordingly so that additional ecological health impacts can be incorporated in their design and implementation (Balvanera *et al.*, 2014).

Figure 6.1 Summary of CAREX science communication and outreach activities in 2016. Figure and numbers prepared by Kristy L. Hogsden.

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